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THE REDUCTION OF AROMATIC NITRO COMPOUNDS
BY SULPHIDE AND HYDROSULPHIDE IONS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF

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BY

O.J. COPE

DEPARTMENT OF CHEMISTRY

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As a prerequisite to the study of the reduction of nitro-
ACKNOWLEDGEMENT
benzenes by sulphide and hydrosulphide ions, the composition of

The author wishes to express his grateful appreciation to Dr.R.K.Brown for his enthusiastic guidance and encouragement throughout the course of this work.

ABSTRACT

As a prerequisite to the study of the reduction of nitrobenzene by sulphide and hydrosulphide ions, the composition of sodium polysulphide solutions has been examined. The spectrophotometric methods used indicated that the composition of these solutions is dependent on pH. A method was developed, using spectrophotometric techniques, which allowed the polysulphide produced during the course of nitrobenzene reduction by sulphide or hydrosulphide to be determined. However attempts to adapt this method to the determination of the degree of hydrolysis of these polysulphide solutions, was unsuccessful.

The reduction of nitrobenzene by sodium sulphide in aqueous ethanol has been examined. Both the sulphide and hydrosulphide species are considered to be responsible for the initial very slow reduction with possibly some contribution from traces of polysulphide ions. The reduction is markedly accelerated by the addition of elemental sulphur, which forms poly (probably di-) sulphide, a much more reactive reducing species. The formation of "active" elemental sulphur during the course of the reduction produces disulphide and thus gives rise to an autocatalytic reaction. Some of this elemental sulphur is lost as thiosulphate by reaction with hydroxyl ions produced by the reduction itself, and by hydrolysis of sulphide and disulphide ions. The addition of base increases the rate of reduction due to a shift in the equilibria $S_2 + H_2O \rightleftharpoons HS^- + OH^-$ and $S_2 + H_2O \rightleftharpoons HS^- + OH^-$, but this is offset by greater loss of the active elemental sulphur as thiosulphate, thus decreasing the autocatalytic acceleration of rate.

The reduction of nitrobenzene by sodium hydrosulphide and hydrodisulphide in aqueous media has also been examined. Nitrobenzene is reduced by the HS^- ion initially as far as phenylhydroxylamine which is then reduced by HS_2^- much more slowly than is nitrobenzene. As the reaction progresses HS_2^- is formed which, along with the small concentration of S_2^- present, is responsible for the observed autocatalysis. However HS_2^- reduces phenylhydroxylamine faster than it does nitrobenzene and thus the phenylhydroxylamine concentration reaches a maximum, thereafter declining. Thus only aniline and some unreacted nitrobenzene are present towards the end of the reaction.

The reduction of phenylhydroxylamine by HS^- to aniline produces $\text{S}_2\text{O}_3^{2-}$ but no detectable amounts of HS_2^- , whereas reduction by HS_2^- involves the conversion of yellow HS_2^- only to the colourless $\text{S}_2\text{O}_3^{2-}$ ion. On the other hand the reduction of nitrobenzene by HS^- and HS_2^- is accompanied by an increase in the HS_2^- concentration besides the formation of $\text{S}_2\text{O}_3^{2-}$. A comparison of the rate constants shows that under the reaction conditions, HS_2^- (with the trace of S_2^- presumably present) reduces nitrobenzene about seven times faster than the HS^- ion. Phenylhydroxylamine is reduced two to three times more rapidly by HS_2^- (and the trace of S_2^- present) than is nitrobenzene.

Using the appearance of polysulphide as a measure of the rate of reduction, a comparison of the relative reduction rates of p-alkylnitrobenzenes by hydrosulphide ion has been carried out, where the alkyl substituents were methyl, ethyl, i-propyl and t-butyl. A Baker-Nathan order was observed and the results are discussed in terms of hyperconjugation and solvent effects.

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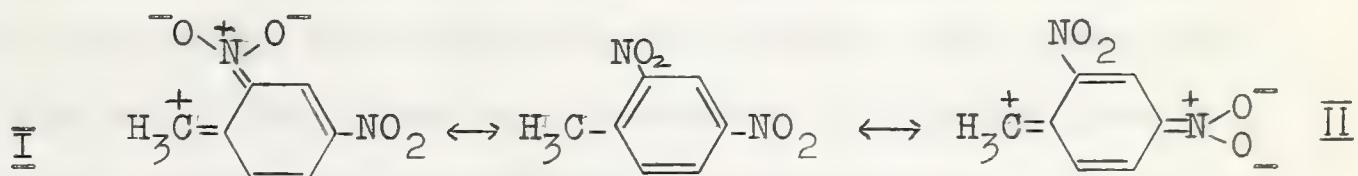
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INTRODUCTION

PREAMBLE

The genesis of this thesis was an attempt to rationalize the selectivity observed in the reduction of various aromatic polynitro compounds by sulphide and disulphide reducing agents. Specifically, 2,4-dinitrotoluene on reduction with ammoniacal hydrogen sulphide at room temperature gives predominantly the 4-amino-2-nitro product in 80% yield (1). However, reduction with stannous chloride in acid medium provides the 2-amino-4-nitro isomer (2), although Blanksma reports the formation of some of the 4-amino-2-nitro compound as well (3). Hodgson attempted to explain the selectivity observed by invoking the Baker-Nathan effect (4).

He postulated that the hyperconjugative effect of the methyl group in 2,4-dinitrotoluene is greatly assisted by the two nitro groups which are in the ortho and para positions to it. As a result, two possible resonance or contributing forms, one for the ortho and one for the para quinonoid structure, can be written for the molecule as shown below:



Structure II will predominate owing to its greater stability. According to Hodgson (5) the ease of reduction of the nitro group is dependent on the ease of detachment of oxygen from the nitro group, and this in turn is facilitated the more negative the nitro group is. Hence, as the resonance structure II predominates the 4-nitro group will be relatively more negative and therefore

more easily reduced. Hodgson employs the term "negative" and "positive" as synonyms of nucleophilic and electrophilic, respectively.

In acid solution, Hodgson presumes the hyperconjugative effect to be at a minimum; and thus the electron release of the methyl group is primarily inductive in nature. Thus the 2-nitro group will be more negative than that in the 4 position and, as a result, more susceptible to protonation. The highly positively charged group resulting is then preferentially reduced by the acid stannous chloride. In other words, the foregoing explanation is contingent upon Hodgson's hypothesis that a relatively negative nitro group is more susceptible to reduction by sulphide ion; whereas a relatively positive nitro group is more easily reduced by acid stannous chloride.

However, the bulk of experimental evidence in the literature would seem to cast doubt on the validity of Hodgson's rationale. Firstly, the fact that 2,4-dinitro-t-butylbenzene is also selectively reduced by sulphide to the 4-amino-2-nitro compound (6 and 7) cannot be explained by a similar recourse to hyperconjugation. Secondly, the reduction of aromatic nitro compounds is facilitated by the presence of electron withdrawing groups in the molecule, whether the reduction is acid stannous chloride (8) or sodium disulphide (9). In fact, Ogata (10) reports the very large positive Hammett ρ value for the disulphide reduction of nitro compounds of +3.55. Thus, the attack of the sulphide ion or disulphide ion is at a site of relatively low electron density; and, a priori, this may be on the nitrogen atom or on one of the oxygen atoms of the nitro group.

It would seem necessary in order to evolve a general theory of selectivity in the reduction of aromatic polynitro compounds that the interplay of various factors must be taken into consideration. Thus, in addition to electronic effects, steric considerations not only of the substituents but of the reducing species itself are doubtless important. For instance, Verkade (12) found that sodium disulphide reduction of 2,4-dinitroanisole gave a ratio of the 2-amino-4-nitro isomer to the 4-amino-2-nitro isomer of 4:1, whereas the corresponding ratio for reduction of 2,4-dinitroisopropoxybenzene was 0.9:1. In this case, at least, the large change in isomer ratio would be attributable to the bulky nature of isopropyl group compared with that of the methyl group. Also, to a lesser extent, the nature of the solvent appears to be important since Verkade (12) found that the reduction of 2,4-dinitro-n-propoxybenzene with disulphide gave an isomer ratio of 1.7:1 in completely aqueous medium and 1.55:1 in ethanol.

Schröter's (13) excellent review of the reduction of nitro compounds gives many examples of selective reduction of dinitro compounds where the nitro groups are ortho, meta or para to one another. A superficial examination of these uncovers no obvious simple relationships that would allow one to predict the course of selectivity in a particular case.

1. The Problem

It was decided that a prerequisite to any general theory explaining the foregoing selective reduction was a study of the reduction process itself.

The following work, therefore, has been limited to an examination of nitrobenzene reduction by sodium sulphide in aqueous

ethanol and to the reduction of nitrobenzene by sodium hydrosulphide in aqueous solution. These specific cases were chosen, in the first place, because they have, to date, received relatively little detailed study. Also, it was thought desirable to conduct these reduction studies under conditions likely to be employed in preparative work. Thus, the observations made here would be of some practical value in assessing optimum reaction conditions for sulphide and hydrosulphide reductions in synthetic work.

As the complexity of the monosulphide reduction was shown to be partly due to its high and changing pH, it was decided in the case of the sodium hydrosulphide reduction to use a solution with some buffering capacity. To this end the sodium hydrosulphide was prepared by adding slightly over one molar equivalent of ammonium chloride to it. This system has been used before in preparative work as will be discussed later and theoretically corresponds to ammonium hydrosulphide, also commonly used in preparative work. In order to test the sensitivity of the method evolved here for following reduction rates using sodium hydrosulphide, a comparison of the relative rates of reduction of p-alkyl nitrobenzenes was undertaken (where the p-alkyl group was methyl, ethyl, isopropyl and tertiary butyl). In attempting the same comparison using sodium sulphide as the reducing agent, p-nitrotoluene suffered oxidation to some extent, causing interference with the expected course of the reduction. This will be discussed in more detail below both in the literature survey and in the experimental section. The results obtained from the comparative reduction rates would allow some deductions to be made

as regards the electron releasing abilities of the various alkyl groups in such a system; in other words a system where the activated complex formation is favoured by electron recession from the reaction centre.

As will be pointed out later, hydrosulphide reduction of mononitro compounds often leads to N-substituted hydroxylamine formation. Thus it was necessary to establish the nature of the final reduction product and also of any intermediate reduction products formed in significant concentrations during the course of the reaction.

In addition to the foregoing work an attempt was made to develop a photometric method for determining the concentration and degree of hydrolysis of polysulphide solutions. As a result of this work several important implications have emerged as to the nature of such polysulphide solutions.

The review of the literature pertinent to this thesis has, of necessity, had to be expanded to include an examination of the literature concerned with the constitution of polysulphide solutions. Examples of sulphide and hydrosulphide reductions in the literature are examined as regards reaction conditions and the nature of both organic and inorganic reaction products.

2. Literature Survey

Constitution and Degree of Hydrolysis of Sodium Sulphide and Polysulphide

During the course of this work Ogata (10) published his work on the disulphide reduction of nitrobenzene in aqueous methanol at 50°C. Bullock and Forbes (1) previously had studied in some detail the disulphide reduction of sodium m-nitrobenzenesulphonate

in water at 25°C. Thus, the present work was confined to a study of the reduction of nitrobenzene by sodium sulphide and also by sodium hydrosulphide. However, as polysulphide was generated during the course of both these reductions, it became necessary to have some understanding of the nature of polysulphide solutions.

Although various studies have been made of the nature of polysulphides (14) (15) (16), the subject is still not fully understood; and, in fact, the literature contains some apparent contradictions.

There is general agreement on the fact that the various polysulphide ions, $S_x^{\frac{2}{x}}$ (where in aqueous solution $x = 2$ to 5), exist in mobile equilibrium with one another. However, Gerischer (17) by measuring the rates of solution of sulphur in various polysulphide solutions of composition $S_x^{\frac{2}{x}}$ (where x is 1 to 4) found that solution took place most quickly when $x = 2$. Thus one would expect that in a reaction where sulphur is formed in situ, as in sulphide reductions, that the disulphide initially formed would compete more effectively for sulphur than does the original monosulphide. Thus $S_3^{\frac{2}{3}}$ would tend to accumulate. However, this does not necessarily contradict the conception of a mobile equilibrium between the polysulphide ions; as it is conceivable that, although $S_3^{\frac{2}{3}}$ is kinetically preferred, subsequent establishment of thermodynamic equilibrium may give rise to the normal position of mobile equilibrium between the various polysulphide species. However, Gerischer's work suffers from the uncertainty common to much of the work in this field: - that is, doubt as to the exact constitution of initial polysulphide. Thus, the dissolution of 1 molar equivalent of sulphur in a molar solution

of sodium monosulphide would not give a one molar solution of disulphide ion, if the concept of a dynamic equilibrium is to be maintained. In fact, appreciable quantities of $S_3^=$, $S_4^=$ and $S_5^=$ may be present depending on the equilibrium constants involved. Pearson (14) has suggested that $S_3^=$ is relatively unstable, because of the tendency of sulphur to give higher polysulphides than $S_3^=$ when dissolved in sodium sulphide solution. Moreover, it is less thermally stable than the other polysulphides. On the other hand Pearson considered $S_2^=$ to be relatively stable because of the covalent bond between the two sulphur atoms. Likewise he suggested that $S_4^=$, because of its symmetrical structure, $(S \leftarrow S - S \rightarrow S)^=$ was relatively stable. As $S_5^=$ is known to be quite stable, Pearson suggests a structure of the type $(S \rightarrow S \rightarrow S \leftarrow S \rightarrow S)^=$ to explain this. However, there is no other evidence in the literature to support the existence of a 5-membered ring in the $S_5^=$ ion.

Pearson also prepared Na_2S_6 in absolute ethanol. And, as addition of water to this caused a quantitative precipitation of one atom equivalent of sulphur, it appears that $S_5^=$ is the highest polysulphide stable in aqueous medium. It is of interest to note that polysulphides up to $S_7^=$ have been prepared from metallic sodium and elemental sulphur in liquid ammonia (18). Also it is claimed that a compound of the definite composition Na_2S_3 can be prepared directly from its elements under boiling toluene (19). Nevertheless, the transference of polysulphide of known composition in non-aqueous medium to aqueous medium could introduce the possibility of the establishment of a mobile equilibrium and, therefore, an uncertainty as to composition.

Peschanski (15a) also has shown that "polysulphide" concentration is linearly proportional to the quantity of sulphur dissolved in sodium sulphide, and that x in Na_2S_x reaches a maximum of five in water. Furthermore, the pH was found to be independent of concentration of sodium polysulphide in the range between 0.4 and 0.8 M for the various polysulphide solutions. Also a marked "buffer" effect was noted for Na_2S_x where $2 \leq x \leq 4$, resulting in very little change in pH with increasing sulphur content from Na_2S_2 to Na_2S_4 . In a subsequent paper, Peschanski (15b), from pH measurements using a glass electrode and redox potential measurements made against a normal hydrogen electrode, was able to calculate a likely distribution of the different polysulphide ions in various polysulphide solutions. The following results are given for a 0.456 M solution. The first example 1. is for what is normally assumed to be Na_2S_2 (here x actually = 1.96).

	SH^-	$\text{S}^=$	$\text{S}_2^=$	$\text{S}_3^=$	$\text{S}_4^=$	$\text{S}_5^=$
1.	0.280	0.004	0.053	0.076	0.035	0.008
2.	0.314	0.006	0.035	0.055	0.018	0.003

and the second example is for a Na_2S_x solution where $x = 1.45$.

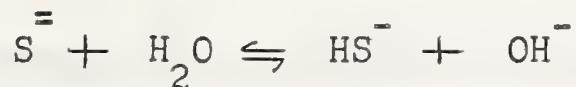
Before considering these results, the following sources of error must be borne in mind. Firstly, no effort was made by Peschanski to avoid air oxidation; although the author reports that such a reaction took place to give thiosulphate ion. Secondly the value of pK_2 for hydrogen sulphide of 14.9 used in Peschanski's calculations is of doubtful accuracy as will be seen in a subsequent discussion below. No reference was given for the value used; and, furthermore, it involved only one significant figure.

Moreover, the results obtained do not take into consideration the species S_xH^- where $x > 1$. However, assuming the validity of the final results, the first surprising fact is the high concentration of $S_3^=$ in both cases. This would seem to contradict Pearson's (14) observation that $S_3^=$ is relatively unstable as compared to $S_2^=$ and $S_4^=$. Another unexpected feature of these results is the relatively low concentration of $S_5^=$, which in example 1, is actually lower than the concentration of $S_5^=$ present.

It may nevertheless be reasonable to suppose that at lower concentrations of dissolved sulphur, e.g. where x in Na_2S_x lies between 1.0 and 1.1, the predominating polysulphide species are $S_2^=$ and $S_3^=$. If these two ions have comparable reducing abilities, the overall kinetic picture becomes less complicated.

Degree of Hydrolysis of Sodium Sulphide

It is well known that sodium sulphide is extensively hydrolysed in aqueous solution according to the equation:



and Kuster and Heberlein (23) indicate 50% hydrolysis for one molar sodium sulphide. In order to calculate the degree of hydrolysis, the second ionization constant of hydrogen sulphide has to be known with some degree of accuracy. Unfortunately, there is considerable disagreement in the literature as to its value (20) and (21). Kubli has reviewed the literature and found values of pK_2 ranging from 13.22 to 14.92. Taking into consideration the activity of the hydroxyl ions in solution,

and using special electrodes to measure the pH of the solutions, he has obtained a value of $12.44 @ 20^{\circ}\text{C}$ (22).

Ogata et al. state that the hydrolysis constant of sulphide ion in aqueous solution is approximately 10. However, no reference source is given; and presumably the values of $K_w = 1 \times 10^{-14}$ and K_2 for hydrogen sulphide of 1×10^{-15} have been used. It is evident that small errors in the measurement of K_2 will produce relatively large errors in the hydrolysis constant and thus in any estimation of the degree of hydrolysis of aqueous sodium sulphide solutions. Two further complicating factors now arise in the present work. Firstly, as the solution is at 50°C , the value for K_2 must be determined at that temperature. Secondly, as the reaction solvent is aqueous ethanol, the meaning of pH under these circumstances becomes a little vague. Thus, it was deemed necessary to make pH measurements of the sodium sulphide solutions in question at 50°C , and it is believed that the hydroxyl ion activity and alcohol effect have been successfully taken into consideration.

No measurements of the ionization constants of hydrogen disulphide are available in the literature as far as this author is aware. Ogata, in his work, has made a speculative guess as to the magnitude of the corresponding hydrolysis constant ($K_h = 2$); but even this is based on the assumption that the value of the hydrolysis constant for sulphide ion is 10.

Kuster and Heberlein (23) have measured the extent of hydrolysis for a 0.05 molar aqueous solution of Na_2S_x , where x varies from 1 to 5, and claim a decreasing tendency to hydrolysis with increasing sulphur content. Hydroxyl ion concentrations were determined by dilatometrically studying the rate of diacetone

alcohol hydrolysis, which is directly proportional to hydroxyl ion concentration.

Thus, whereas for the monosulphide, hydrolysis occurs to the extent of over 80%, the pentasulphide ion is practically 100% un-hydrolysed. On this scale of comparison the disulphide is approximately 60% hydrolysed which would correspond to a hydrolysis constant of 0.045. However, again the question arises as to whether the supposed disulphide is in fact only disulphide or whether the hydrolysis measured is not in reality a composite, resulting from the various polysulphides present.

In the present work it was found that the pH of a 0.16 M solution of sodium sulphide underwent no detectable change after an equimolar quantity of sulphur was dissolved in it. However, at these high hydroxyl ion concentrations relatively large changes in degree of hydrolysis produce correspondingly very small changes in pH.

Despite the lack of precise data on this question, one fairly certain fact emerges. This is, that in the system under study in this work, the sulphide ion initially present and the polysulphide ions subsequently formed are hydrolysed to a large, though undetermined, degree. Thus, at least four possible reducing species are present at any given time after the inception of the reaction viz. $S^{\frac{2}{2}}$, $HS^{\frac{1}{2}}$, $S_2^{\frac{3}{2}}$ and $HS_2^{\frac{1}{2}}$ ions. If Peschanski's deductions are valid then, of course, the presence of higher polysulphides than $S_2^{\frac{3}{2}}$ is possible. This complex situation is somewhat simplified by the far superior reducing ability of the disulphide ($S_2^{\frac{3}{2}}$) ion over the others as will become evident in the subsequent examination of the experimental results.

Despite the fact that an equilibrium between the various polysulphide species seems to be generally accepted, most authors assume that only disulphide is formed when an equivalent of sulphur is dissolved in sodium sulphide. There are numerous examples of this assumption where disulphide is used in preparative work in ethanolic (24) and (25) and in aqueous medium (26) and (27). Whereas, presumably the constitution of the polysulphide used in these cases is not of great importance from a preparative point of view, in a kinetic study the exact nature and variety of the reducing species used is definitely of some concern. However, Ogata et al. (8) and Bullock and Forbes (9) both assume their reducing species to be only $S_2^=$, although the former workers use aqueous methanol and the latter only water as the reaction solvent. It is probably useful at this stage to summarize the findings of these two workers, as some of their results are pertinent to the present work.

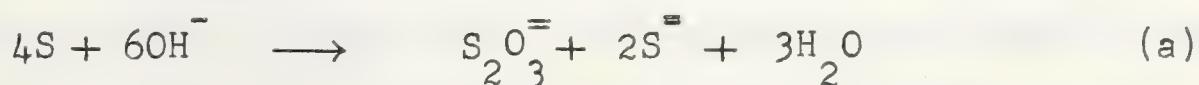
Reduction by Sodium Disulphide

In the first place a study of the reduction by sodium sulphide was abandoned by Ogata as being too slow to follow kinetically. Bullock and Forbes, however, conducted a cursory investigation of the reduction of sodium meta-nitrobenzene sulphonate with sodium sulphide and hydrosulphide and discovered the autocatalytic nature of these reductions. Ogata et al. apparently did not refer to the work of Bullock and Forbes. The latter demonstrated that the reduction of the nitro compound was first order with respect to nitro compound and second order with respect to disulphide ion. However, when allowance was made

for hydrolysis by making the solution 0.75 M in sodium hydroxide, essentially buffering hydrolysis of the disulphide, they were able to show that the reduction was actually first order with respect to the disulphide ion itself.

It is rather surprising that, without taking this hydrolysis into account, Ogata et al. found an exact second order relationship in their work; while Bullock and Forbes observed a first order relationship. In addition, Ogata et al. took no direct precautions to eliminate oxygen from their system. They did in certain cases make corrections for air oxidation by the use of blank experiments, although this failed to correct a divergence from the rate constants found in other runs by a factor as high as 6.

Bullock and Forbes maintained a stream of nitrogen over the reaction mixture in their experimental work. In the present work it was found that sodium sulphide solutions of sulphur are extremely sensitive to air oxidation, and that it was necessary not only to keep the reaction mixtures under a nitrogen atmosphere but to deaerate all reaction solvents prior to use. In Bullock and Forbes' work the chief product of disulphide oxidation by nitro compound was thiosulphate, which was shown to have arisen indirectly through the reaction of sulphur formed from the initial reduction with the hydroxyl ion also generated according to equations a and b



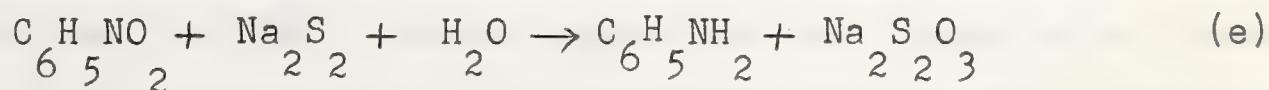
However, higher polysulphides are almost certain to have been formed initially, as some of the sulphur formed in situ would easily react with disulphide as shown in equation c and d.



They did in fact note that the colour of the reaction mixture intensified, this yellow colour being a characteristic of polysulphide solutions.

Another possible source of error in their analyses was their iodometric determination of thiosulphate ion following the precipitations of sulphide with cadmium carbonate. The hydroxyl ions generated during the reaction would not have been removed from solution using this procedure. Presumably this fact was appreciated, for in a subsequent stage of product analysis sulphide ion was precipitated with cadmium carbonate and the remaining solution titrated with standard acid to demonstrate a large increase in hydroxyl ion concentration. Since iodine's colour is discharged instantly upon reaction with hydroxyl ion, failure to remove hydroxyl ions would result in an inaccurate estimation of thiosulphate and sulphide ions by this technique.

Bullock and Forbes further established that no sulphite ion was formed and that the only reduction product was the amine. Ogata et al. similarly were able to demonstrate that the amine was the only product of nitro compound reduction. They, however, undertook no examinations of the inorganic components of the system and apparently assumed that the trivial stoichiometric equation



represented the full course of the reaction.

Sodium Sulphide as a Reducing Agent

Sodium sulphide is not as highly favored in preparative work as is the polysulphide which reacts much more quickly, or as is the hydrosulphide which can be used where a low hydroxyl ion concentration is required. However, there are many examples of its use in the literature for the reduction of mononitro compounds (1) and (28,a-f). The products in the references given are amines in each case. In the present work involving the sodium sulphide reduction of nitrobenzene in aqueous ethanol at 50° C only aniline was detected as a reduction product.

The well known scheme of stepwise reduction of aromatic nitro compounds indicated by Haber's (29) work is shown in equation f.



However, an alternative route of a competing condensation reaction between the nitroso compound and N-phenylhydroxylamine to give an azoxy compound is possible.



The kinetics of this condensation have been studied by various workers (30), (31) and (32), and it has been shown to be a fast reaction which is very strongly catalyzed by hydroxyl ions. However, the absence of any bimolecular condensation products in the present work indicated that either the N-phenylhydroxylamine was reduced by the sulphide or polysulphide ion almost as fast as it was formed, or that nitrosobenzene was not formed as an intermediate in this reduction. This must also have held in Ogata's work

where no azoxy formation was observed. In their case a cursory examination of azoxybenzene reduction by sodium disulphide showed it to be reduced 10 times more slowly than the nitrobenzene and thus, its presence amongst the products would be expected if this reaction sequence were operative. A similar experiment in the present work suggested that the reduction of azoxybenzene with sodium sulphide is very slow and only proceeds as far as azobenzene. Thus, its presence would easily have been detectable.

As mentioned before, Ogata et al. considered the nitrobenzene reduction by monosulphide to be too slow to follow kinetically, and Bullock and Forbes demonstrated the autocatalytic nature of this reduction in the case of sodium *m*-nitrobenzene sulphonate. Rashevskaya has suggested from a study of the sodium sulphide reduction of nitro compounds at 50°^oC that the sulphide is first oxidized to the tetrasulphide. The latter, in the presence of sodium hydroxide, will also reduce the nitro compound, and in doing so is itself oxidized to thiosulphate ion (33). Hodgson (34) has proposed a mechanism for hydrosulphide reduction of nitro compounds which is extremely speculative in nature and involves attack of the negatively charged reducing species directly on the relatively negatively charged OXYGEN of the nitro group. The mechanism does not explain the observed increase of pH during the reaction; nor does it account for the intensifying of yellow colour during the reaction. Presumably, if thiosulphate were to be the only product of hydrosulphide or monosulphide reduction, such reaction mixtures at the completion of reduction should be colourless. This is not the case (see Experimental Results). It is most important to note that examples of

hydrosulphide, sulphide and polysulphide reductions in the preparative literature seldom involved any precautions to exclude air from the reaction mixture. Polysulphide and monosulphide ions are very susceptible to air oxidation; and, thus, the formation of thiosulphate via direct air oxidation of these species cannot be excluded. During the course of this present work, it has been qualitatively shown that bubbling air through such solutions caused a discharge of the characteristic yellow colour of polysulphide and resulted in the formation of thiosulphate ion. From this consideration, and from Bullock and Forbes' work, it would appear that the propensity of such reductions to produce thiosulphate is dependent on the pH of the system. Thus, thiosulphate is favored at higher hydroxyl ion concentrations due to competition by reaction (b). However, from Bohnholtzer and Heinrich's study of the electrolysis of sodium sulphide, the nature of the oxidation products would seem to be dependent on the oxidation potential and nature of the electrodes used (35). Thus, using a bright platinum electrode at low current and low potential, only polysulphide was obtained. When the electrode was coated with finely crystalline rhombic sulphur and the potential kept below 0.1 volts, the sulphur coating dissolved to form polysulphide; again, no other sulphur-containing product was formed. However, at high potentials, sulphate and some dithionate were formed when a bright platinum electrode was used; whereas an electrode coated with sulphur afforded a mixture of polysulphide, sulphate, dithionate and thiosulphate. This further illustrates the complexity of the reduction process.

Reduction by Hydrosulphide Ion

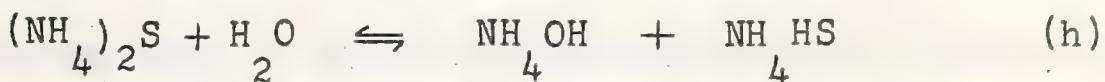
It was decided to study the mechanism of hydrosulphide ion reduction with the view of using this system as a means of comparing the reduction susceptibilities of various substituted nitro compounds.

Because of their high pH, sodium sulphide and disulphide solutions cannot be used with compounds containing easily hydrolyzable grouping such as esters. In addition, due to the high nucleophilicity of the sulphide and disulphide ions, hydrogen or even the nitro group itself can be displaced to give the corresponding thiol, sulphide or disulphide. For example, the sodium sulphide reduction of p-chloro nitrobenzene will give p-aminothiophenol (36) or bis-(p-aminophenyl) monosulphide (37) depending on conditions. Similarly, sulphide reduction of 1,2-dinitronaphthalenes is accompanied by considerable replacement of the 1-nitro group to give the corresponding sodium mercaptide (38). Even attempted sodium hydrosulphide reduction of o-dinitrobenzene yielded almost entirely a mixture of sodium o-nitrophenyl thiol and bis-(o-nitrophenyl) monosulphide (39). However, perhaps the most important side reaction of concern to this work is due to the ability of alkaline polysulphide to oxidize active methylene or methyl groups. Thus, p-nitrotoluene yields varying quantities of p-aminobenzaldehyde, depending on conditions (40) and (41); and bis (p-nitrophenyl) methane is oxidized to 44' - dinitrobenzophenone (42).

Hydrosulphide has been widely used as a reducing agent in various forms for preparative work. Sodium sulphide, to which

a molar equivalent of sodium bicarbonate has been added to lower the pH, has been used by Vorontzov (43). Hodgson, similarly, has used a methanolic solution of sodium sulphide and sodium bicarbonate which, after precipitation of sodium carbonate, gave a sodium hydrosulphide solution (44).

In theory, all so-called ammonium sulphide $(\text{NH}_4)_2\text{S}$ solutions, however much excess ammonium hydroxide is present, should contain practically no sulphide ions at all. This situation arises because of the very high hydrolysis constant for the equilibrium



which is given by $K_h = K_w / K_a K_b$, where K_a is the second ionization constant of hydrogen sulphide and K_b the ionization constant for ammonium hydroxide. From the previous discussion concerning the second ionization constant for hydrogen sulphide, it can be seen that a range of values could be used. However, as in this instance the exact value is not of great importance, the value will be arbitrarily taken as 1×10^{-14} . Using values for $K_w = 1 \times 10^{-14}$ and $K_b = 1 \times 10^{-5}$ a value for K_h of 1×10^5 is obtained. In other words, the equilibrium lies very largely to the right and even very concentrated ammonium hydroxide (16M at a density of 0.90) would have very little effect on this equilibrium. Also, whichever literature value of K_a is used, K_h will still be large.

Murray and Walters (45) and Hartman and Sillaway (46) have employed ammonium chloride and sodium sulphide in equimolar quantities in the presence of excess ammonia. Aqueous ammonia saturated with hydrogen sulphide is also a very common reducing agent and has been used for the reduction of mononitro (47) and poly-nitro compounds (48). Working at lower pH's, hydrogen sulphide in the presence of a low "catalytic" concentration of ammonia or

other strong organic base has given high yields of reduction products (49), particularly in the selective reduction of trinitrotoluene (50). Lowe has published a patent describing the selective reduction of polynitrotoluenes and benzenes with sodium hydrosulphide buffered with ammonium acetate to maintain a pH of about 8. High yields of the corresponding nitro-amines are reported (51).

Nature of Products in Hydrosulphide Ion Reduction

In examining some of the foregoing literature, it was of interest to note what products were obtained from the reduction of nitrobenzenes. In all cases, except for the work of Cohen and McCandlish (49), the amine was obtained as the principal product of nitro compound reduction. Cohen, in reducing nitrobenzene at room temperature with hydrogen sulphide in the presence of a trace of ammonia, obtained N-phenylhydroxylamine. This was borne out by the report of Goldschmidt and Larsen who for the reduction of several nitrobenzenes employed an aqueous sodium hydrosulphide solution through which hydrogen sulphide was bubbled (52). In this manner at room temperature (25°C) N-phenylhydroxylamine was obtained as their chief reduction product of nitrobenzene.

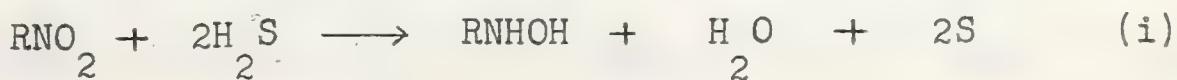
Similarly, Willstätter (53) has reduced nitrobenzene and nitrotoluene to the corresponding substituted hydroxylamines with ammonium sulphide in aqueous ethanol at room temperature. The same results were obtained by Lapworth in aqueous medium (54) where various nitro compounds, including nitrobenzene, were reduced in emulsified form with sodium hydrosulphide to the

corresponding hydroxylamine. The temperature in this case never rose above 30°C and the sodium hydrosulphide was made by adding the requisite amount of the hydrochloric acid to sodium sulphide. It is of interest to note that nitrobenzene has been electrolytically reduced as far as N-phenylhydroxylamine at room temperatures with a cathode potential of 6 - 8 volts (55).

The evidence so far seems to indicate that hydrosulphide reductions at ambient temperatures only proceed as far as the corresponding phenylhydroxylamine. At higher temperatures the amine is often obtained. Thus, at 50°C p-nitrophenylacetic acid is reduced completely to the amine, using ammonium sulphide (47) or sodium sulphide-ammonium chloride solution (45). However, even at low temperatures, under certain conditions reduction to the amine can take place. Thus aqueous pyridine saturated with hydrogen sulphide reduces nitrobenzene even at 0°C (56) to give a 65% yield of aniline after four hours. On the other hand in this last-mentioned case, the pyridine also served as the solvent, for 2 moles of pyridine were used for each 0.1 mole of nitro compound and less than 0.4 mole of water was present.

Oxidation Products of Hydrosulphide Ion

At the low pH's encountered in the foregoing examples, the sulphur initially produced by oxidation of the hydrosulphide ion was precipitated as such. Thus, under the conditions employed by Goldschmidt and Larsen, a more than quantitative precipitate of sulphur was obtained on the basis of the equation:

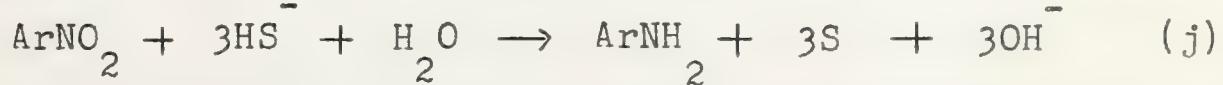


In fact the ratio of gram-atoms of sulphur produced to moles of nitrobenzene reduced was 2.14:1. This implies that about 14% of the hydroxylamine was further reduced, probably to the amine, although no mention was made by these workers of the production of amine (52).

Likewise, under the conditions employed by Jozkiewicz (56) hydrogen sulphide was quantitatively oxidized to sulphur. However, in both Lapworth's and Willstätter's work, thiosulphate ion was formed in addition to polysulphide. This latter substance was characterized by the development of its yellow colour. As mentioned before, Hodgson's proposed mechanism of reduction by hydrosulphide allowed only for thiosulphate as the product of hydrosulphide ion oxidation. Brand (1) likewise found that the hydrosulphide reduction of various dinitro compounds gave thiosulphate as the principal hydrosulphide oxidation product.

Goldschmidt (52) observed that reduction by sulphide or polysulphide in the absence of hydrogen sulphide gave rise to thiosulphate. This, he argued, was of secondary origin due to reaction between initially formed hydroxyl ions and higher polysulphides. This agreed with Bullock and Forbes' conclusions. If this is the only source of thiosulphate ion, then its formation at low pH would not be expected.

On the other hand, if the nitro compound concentration is sufficiently high relative to the hydrosulphide ion concentration, the generation of hydroxyl ions according to the equation:



may cause a sufficient increase in pH to make thiosulphate

formation important.

On this basis, Schröter's comment (13), that the lower pH encountered in sodium hydrosulphide and ammonium sulphide reductions is responsible for thiosulphate formation is difficult to rationalize.

SECTION 2.

RESULTS AND DISCUSSIONS

PART I

The Constitution of Sodium Sulphide and Sodium Polysulphide in
Aqueous Ethanolic Solution

Before any consideration could be given to a kinetic study of the reduction of nitrobenzene with sodium sulphide, it was first necessary to examine the constitution of aqueous ethanolic solutions of sodium sulphide used in this work. In particular a knowledge of the extent of hydrolysis of sodium sulphide under these conditions (viz. in aqueous ethanol solution at 50°C) was required to determine the relative concentrations of sulphide and hydrosulphide ion in solution. Since polysulphide appeared during the course of the reduction of nitrobenzene with sodium sulphide and proved to be responsible for most of the reduction, an attempt was made to characterize polysulphide solutions where sodium sulphide was present in large excess.

A. The extent of hydrolysis of (1) sodium sulphide and (2) sodium polysulphide in aqueous ethanol from pH measurements

1. Sodium Sulphide Solutions

In view of the variety of values given in the literature for the second ionization constant of hydrogen sulphide, it was decided to measure the pH of the reduction solutions directly. The aim was to obtain at least a rough estimate of hydroxyl ion concentration in the reaction solutions, making allowance for the

fact that the solvent was not water. It was observed that a 0.160 M solution of sodium sulphide in the 40% by weight aqueous ethanol had a pH of 12.60 at 50.0°C. A similar solution in water had a pH of only 12.00 at 50.0°C.

A series of sodium hydroxide solutions were prepared, and two aliquots of each were diluted, so as to give two solutions, one completely aqueous, and the other 40% by weight aqueous ethanol. The concentration of sodium hydroxide in each was then the same, although no effort was made to determine the exact concentration in each case. The pH of each solution was measured at 50°C and the following results obtained:

pH at 50°C	
Water	Aqueous Ethanol
11.80	12.40
12.00	12.60
12.10	12.70
12.40	13.00
12.60	13.20
12.70	13.30
13.00	13.60

A constant difference of 0.60 pH units was at once discernible and could be expressed as $pH_{H_2O} = pH_{H_2O - alcohol} - 0.060$. The "alcohol effect" on pH readings obtained for solutions in aqueous alcohol has been recorded previously (59). It is seen that a knowledge of the concentration of sodium hydroxide in water and the pH to which it corresponds can be used to estimate the concentration of sodium hydroxide in an alcohol-water mixture by measurement of the pH of the latter solution. In this manner, advantage can be taken of the known values of pK_w in water for conversion of pH to pOH , and hence to hydroxyl ion concentration.

Thus, the 0.160 M solution of sodium sulphide having a pH of 12.60 in aqueous ethanol and 12.00 in water alone, has a hydrogen ion concentration of $10^{-12.00}$. Using $pK_w = 13.26$, the value reported for a temperature of 50°C (60), the hydroxyl ion concentration of $5.5 \times 10^{-2}\text{M}$ is obtained. The pH readings were considered to be accurate to ± 0.02 units, hence the hydroxyl ion concentration was expressed as $0.055 \pm 0.002\text{ M}$.

A further complication arose from the fact that as pH is a measure of hydrogen ion activity and not the actual hydrogen ion concentration, the activity coefficient of sodium hydroxide at these concentrations and temperatures must be known. The activity coefficient of 0.1 molal solution of sodium hydroxide in water at 25°C is 0.766 (60). However, lacking such data for 50°C , the pH of a 0.050 M solution of sodium hydroxide in water was measured at 50°C and found to be 11.90. The calculated value, using pK_w at $50^\circ\text{C} = 13.26$, is 11.96. This corresponds to an activity coefficient of 0.88, which when applied to the hydroxyl ion activity of 0.055 obtained above, gave an actual hydroxyl ion concentration of $0.063 \pm 0.002\text{ M}$.

On the basis of the above calculations, the extent of hydrolysis of a 0.160 M solution of sodium sulphide in the aqueous ethanol at 50°C was estimated to be $39 \pm 2\%$. The sulphide ion concentration in the reduction mixtures studied was therefore $0.097 \pm 0.002\text{ M}$. From these figures a value of 4.1×10^{-2} was obtained for the hydrolysis constant of sodium sulphide in the aqueous ethanol at 50°C . It is realized that these calculations are approximations, but they do supply, at least, a rough estimate of the sulphide ion concentration.

2. Sodium Polysulphide Solutions

It was initially anticipated that a similar treatment to the one outlined above for sodium monsulphide could be applied to the disulphide. However, measurement of the pH of a 0.160 M sodium sulphide in aqueous ethanol and of the same solution with an atomic equivalent of sulphur dissolved in it, showed no significant difference between the two solutions. A value of 13.40 was observed for both solutions at 25°C. This was surprising, as it was expected that H_2S_2 would be a stronger acid than H_2S even in its second ionization constant; which in turn should result in Na_2S_2 being less hydrolysed than is Na_2S . Although the experiment was repeated several times and different electrodes used for the pH measurements, no difference could be detected between the two solutions. However, as pointed out previously, relatively large changes in degree of hydrolysis at these high hydroxyl ion concentrations produce relatively small changes in pH. When the above solutions were both diluted to about 0.0096 M, the pH of sodium sulphide solution was 12.50; whereas, that for the disulphide solution was 12.40. Although a difference was discernible at this concentration it was obvious that pH measurements constituted an unsatisfactory method for accurate determination of the relative hydrolysis constants of sulphide and disulphide ion.

It is of interest to note that a 0.160 M sodium polysulphide solution corresponding to Na_2S_3 in the aqueous ethanol at 25°C had a pH of 12.15. This represents a significant difference in degree of hydrolysis of the two solutions and corresponds to hydrolysis constants differing by a factor of about 10.

B. The constitution of polysulphide from absorbance measurements

Although the literature indicates uncertainty as to the composition of polysulphide (see Introduction), it can be argued that the polysulphide solutions under study in this work constituted a special case. In other words, as the sulphur content in the formula Na_2S_x was within the limited range $1 < x < 1.1$, it might be expected that the polysulphide under these conditions is mainly in the form of the simplest polysulphide, $\text{S}_2^=$. Corroborative evidence was supplied for this in the form of the Beer's law plot obtained when the concentration of sulphur dissolved in a 0.160 M sodium sulphide solution (solvent - 40% by weight ethanol in water) was plotted against absorbance at $450\text{m}\mu$. (see Experimental section, Fig. 19.) The extinction coefficient obtained from this Beer's law plot was 25. at 25°C . Moreover, the dissolution of one atom equivalent of sulphur in 0.050 M sodium sulphide in aqueous ethanol gave a solution also having an extinction coefficient of 25.

It seems likely that the linearity observed between absorbance and concentration of dissolved sulphur should be due to the presence of only one polysulphide species, presumably the disulphide. If progressive addition of sulphur up to an equivalent of the sodium sulphide present were to produce a parallel change in distribution of polysulphide, favoring the higher polysulphides at higher sulphur concentrations, then the Beer's law plot would have been obtained only if the higher polysulphides have the same extinction coefficient as $\text{S}_2^=$; due allowance being made for the number of sulphur atoms per ion.

However the solution corresponding to Na_2S_3 made by dissolving two atom equivalents of sulphur in 0.050 M sodium sulphide had an optical density of 2.60, viz. an extinction coefficient of 52. This value is slightly more than twice that obtained for Na_2S_2 . In order to bring the absorbance values into a range allowing more precise readings, the solution corresponding to Na_2S_3 was diluted by a factor of 3. The absorbance of the resultant solution was 1.165. corresponding to an extinction coefficient of 70. This very surprising result of an increase in extinction coefficient arising from a decrease in concentration suggests that any equilibrium existing between the various polysulphide species is dependent on the total polysulphide concentration.

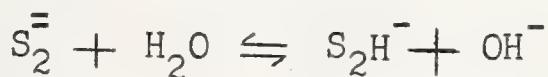
It is possible that at concentrations of 0.160 M the extinction coefficient of the solution corresponding to Na_2S_2 is different from either of the preceding values, but due to the very high absorbance encountered at these concentrations, this could not be measured.

A 0.05 M solution corresponding to Na_2S_4 after threefold dilution gave an absorbance of 2.25, which is about twice that found for the corresponding Na_2S_3 solution. Thus, although the Beer's law plot does not necessarily indicate the absence of the $\text{S}_3^=$ ion, a consideration of extinction coefficients precludes the presence of the $\text{S}_4^=$ ion at the sulphur concentrations indicated in the Beer's law plot. As previously observed, the species referred to here as $\text{S}_3^=$ and $\text{S}_4^=$ may indeed be equilibrium mixtures containing even higher polysulphides and only stoichiometrically corresponding to the species indicated. The increase in extinction coefficient per dissolved sulphur atom in going from $\text{S}_3^=$ to $\text{S}_4^=$ may be a

reflection of the lesser extent of hydrolysis of the latter species (23).

C. The effect of changes in pH on the absorbance of polysulphide solution at 450 μ

The addition of sodium hydroxide to a solution of sodium polysulphide in the presence of excess sodium monsulphide caused an increase in absorbance at 450 μ . The results for a typical experiment are shown in Fig. 1, where it can be seen that successive additions of sodium hydroxide finally produced a maximum absorbance unaffected by further basification. This is interpreted as being due to the depression of the hydrolysis of disulphide by the large hydroxyl ion concentration to the point where the disulphide is essentially all in the unprotonated form.



This implies, of course, that the disulphide ion has a larger extinction coefficient than the hydrodisulphide ion.

Pursuing this argument further, it was then proposed to convert a similar polysulphide solution completely to the protonated form by adding sufficient acid. It was anticipated that from the resultant extinction coefficients for the protonated and unprotonated forms, it would be possible to calculate the ratio of disulphide to hydrodisulphide ion at intermediate pHs; particularly, that of the reduction mixtures. However, it was found that the continual lowering of the pH of polysulphide solutions below 12.60 (the pH observed for a 0.160 M solution of sodium sulphide or disulphide in aqueous ethanol at 25°C) produced a continual increase in absorbance. Thus, a solution of sulphur in sodium

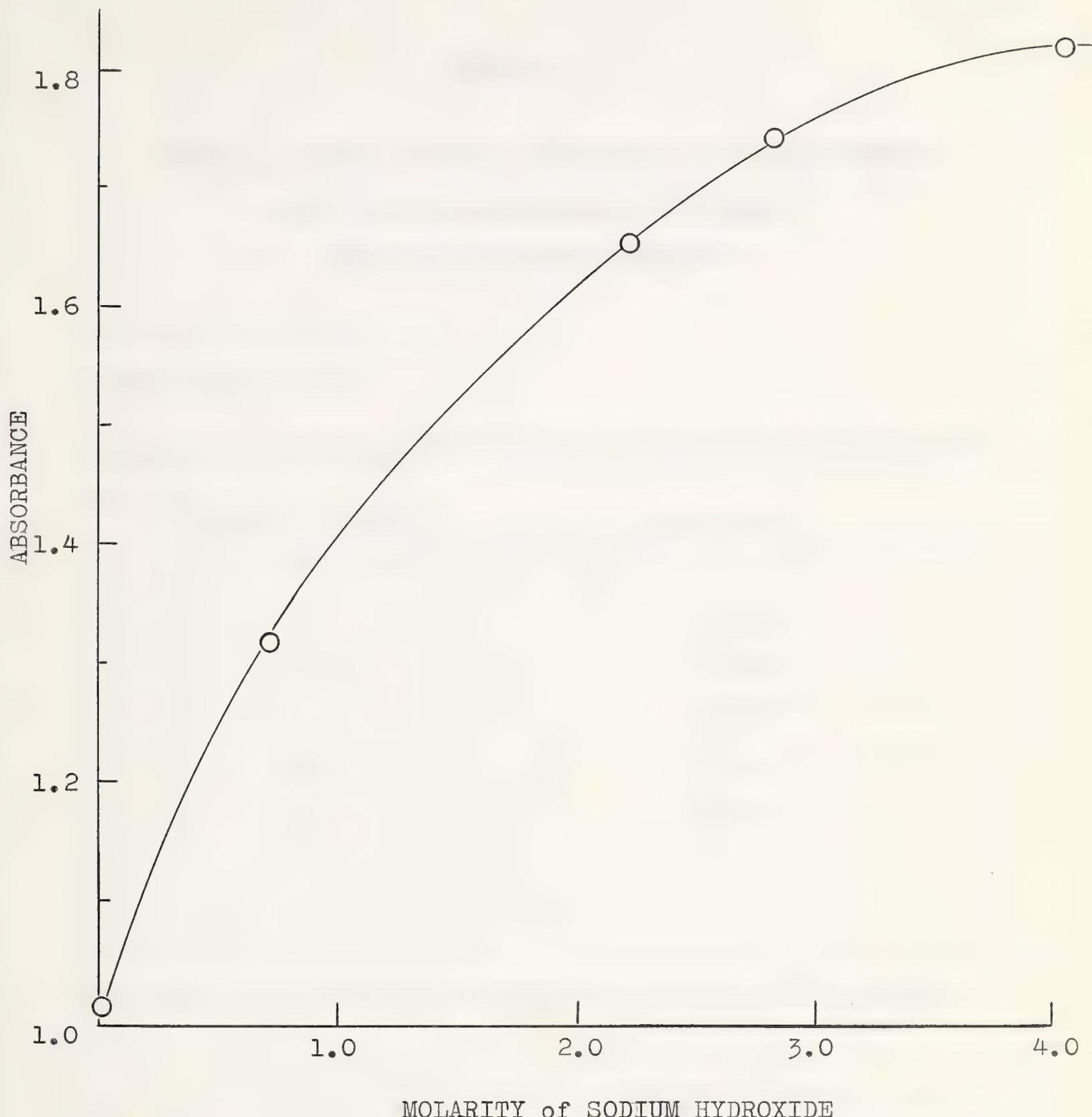


Fig.1. The effect of addition of NaOH on the absorbance at 450 m μ of a solution of sulphur in 0.160 M Na₂S (in aqueous ethanol).

TABLE 1

Effect of Added Sodium Hydroxide on the Absorbance
at 450 mu of a Solution of Sulphur
in 0.160 M Sodium Sulphide

Data plotted in Fig. 1.

Temperature, 25°C.

Molarity of NaOH	Absorbance
0	1.013
0.733	1.320
2.11	1.652
2.81	1.740
4.03	1.82

sulphide corresponding to Na_2S_2 which had an initial absorbance of 0.450 was acidified by the dropwise addition of concentrated hydrochloric acid. The absorbance rose continually to a value of 1.580. Further acidification brought about precipitation of the sulphur. It was found in subsequent experiments that this precipitation took place at a pH of about 7. That chloride ion was not responsible for this increase in absorbance was demonstrated by adding sodium chloride to the polysulphide solution. Even when the solution was almost saturated with sodium chloride (keeping its concentration below that at which "salting out" of the ethanol took place"), there was no appreciable change in the absorbance of the solution.

The addition of sodium bicarbonate, which causes a lowering of pH, also brought about an increase in absorbance of these polysulphide solutions. For instance, the successive addition of sodium bicarbonate to a solution of sulphur in sodium sulphide having an initial absorbance of 1.092, caused the absorbance to increase to 1.700. Further addition of sodium bicarbonate brought about the "salting out" of the ethanol. In a preparation somewhat similar to that used by Hodgson (61) a molar equivalent of sodium bicarbonate was added to a 0.160 M solution of sodium sulphide containing dissolved sulphur and having an absorbance of 0.540. The solution was cooled to below 10°C , and the supernatant liquid filtered free from the precipitated sodium carbonate. The resultant solution, on attaining room temperature (25°C), had an absorbance of 0.640. Great care was necessary to eliminate air in these experiments, as these polysulphide solutions were apparently very susceptible to air oxidation.

A quantitative corroboration of the foregoing observations is found in a comparison of the Beer's law plots shown in Figs. 19 and 20 (see Experimental section). The adherence to Beer's law already observed for solutions of sulphur in sodium sulphide, Fig. 19 is also apparent for sulphur dissolved in sodium sulphide solutions "acidified" with ammonium chloride to a pH of 10.5, Fig. 20. The previously noted extinction coefficient of the former at 50°C is 31.2 whereas that found in the latter case, also at 50°C is 51.3. It is apparent, therefore, that the extent of polysulphide hydrolysis cannot be gauged employing the absorbance measurements and reasoning previously outlined. However, it is of some interest to speculate as to the cause of the higher absorbances noted at low pH's in view of the high absorbances also noted when the solutions are basified. It is conceivable that at these lower pH's the dynamic equilibrium between the various protonated polysulphides is quite different from that found in normal polysulphide solutions.

This may in fact be the case, as Pearson claimed (14) that the dissolution of sulphur in sodium hydrosulphide gave almost exclusively the tetrasulphide, in contrast to the predominance of disulphide formed when sulphur is dissolved in sodium sulphide. As it has been demonstrated above that the $S_4^=$ species does have a higher extinction coefficient per atom of dissolved sulphur than $S_3^=$ or $S_2^=$, the increased absorbance observed when sodium polysulphide solutions are acidified could be due to the formation of the $S_4^=$ species.

Experiments were conducted for the polysulphide solutions "acidified" with ammonium chloride to determine the relative ab-

sorbances of the higher polysulphides. Thus in aqueous solution at room temperature, a 0.45 M solution stoichiometrically corresponding to NaHS_2 had an absorbance of 2.30, i.e. an extinction coefficient of about 50. A 0.045 M solution corresponding to NaHS_3 absorbed too strongly to be measured, but on dilution to 0.018 M, had an absorbance of 2.55 corresponding to an extinction coefficient of about 140; almost three times that of the NaHS_2 solution. The further dilution of the 0.018 M solution by a factor of two, to give an absorbance of 1.275, demonstrates the absence of the dependence of absorbance on concentration observed in the case of Na_2S_2 and discussed previously.

It is of interest to note the effect of solvent on polysulphide absorbance as demonstrated in Fig.20. The extinction coefficient is raised from 35.0 in water at 50°C to 51.3 in 40% (by weight) aqueous ethanol. Also the dependence of extinction coefficient on temperature is shown by the fact that the value obtained at 25°C of 25.6 (Fig.19) is raised to 31.2 at 50°C (Table 20).

SECTION 2.

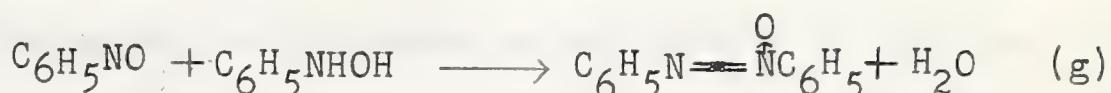
RESULTS AND DISCUSSIONS

Part 11

Product Determination in the Reduction of Nitrobenzene by Sodium Sulphide in Aqueous Ethanol

A. Determination of the course of nitrobenzene reduction by sodium sulphide and nature of the final organic reduction product.

As indicated in the Experimental section, only aniline was found in the work-up of the reaction mixture. This is in agreement with Rashevskaya's findings (33). Under very similar conditions, he was able to recover the corresponding amine in 99% yield from the sodium sulphide reduction of o-nitrophenol, and in 95% yield from sodium m-nitrobenzene-sulphonate. However, this did not necessarily eliminate the possibility that intermediates were formed during the course of the reaction, e.g. azoxybenzene and azobenzene, and subsequently reduced to the amine. That this reaction route, indicated by equation g,



was not competitive with the direct reduction sequence as shown in equation f (see p.15 .) was amply demonstrated in the following ways.

During the course of a typical reduction, aliquots of the reaction solution after dilution were examined spectrophotometrically over the range 200 - 400 $\text{m}\mu$ using a Carey recording spectrophotometer. This was done after 50 minutes, 100 minutes and also after 24 hours. No peaks were observed, other than that ascribed to the nitrobenzene, after any of the times indicated.

Azoxybenzene, azobenzene and hydrazobenzene all absorb strongly in the ultraviolet. In aqueous ethanol (60:40 by weight) azoxybenzene and azobenzene both possess an absorption maximum at 320 m μ , and hydrazobenzene has a peak of 240 m μ and a subsidiary broad band at 290 to 330 m μ . The value for ' ϵ ' of these three compounds is about twice that of nitrobenzene. Thus, the presence of any of these compounds would be easily detected in the presence of nitrobenzene, which has a maximum at 265 m μ . Likewise, during a typical reduction procedure, readings taken at 320 m μ (the λ max. for azoxy and azobenzene) showed a continual fall during the course of the reaction, corresponding to a decrease in nitrobenzene absorbance at that wavelength. Azoxybenzene has been converted to azobenzene by sulphide (57, 58). However, in this work it was found that a 0.005 M solution of azoxybenzene in aqueous ethanol also 0.150 M in sodium sulphide underwent no apparent reduction during the course of 200 minutes at 50° C. The conversion of 2% of the sodium sulphide to disulphide by adding the requisite amount of sulphur caused some reduction to take place. Thus, at the end of 200 minutes, about 1% conversion of the azoxybenzene had taken place as estimated by the decrease in absorbance at 255 m μ . This wavelength corresponds to absorption minimum for azobenzene but a maximum for azoxybenzene. Azobenzene was presumed to have been formed, as the solution developed a distinct orange colour during this time. Hence, even if azoxybenzene were to be formed during the course of nitrobenzene reduction, under these conditions it would not be significantly reduced further. Moreover, any further reduction would proceed only to the azobenzene. As neither of these substances was detected during the reduction of nitrobenzene, it can be concluded that the bimolecular condensation reaction indicated by equation g is insignificant.

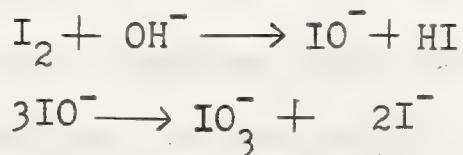
The above results indicated that the course of nitrobenzene reduction went entirely by its direct reduction to aniline, with the possibility, by analogy to Haber's work (29), that nitroso-benzene and N-phenylhydroxylamine were reduction intermediates. However the possibility remained that the reduction of the presumed intermediate, N-phenylhydroxylamine to aniline was slow enough to allow the former to accumulate for at least part of the reaction. This would not be very likely however, if nitroso-benzene were also a reduction intermediate as at these high hydroxyl ion concentrations the N-phenylhydroxylamine condensation reaction with nitrosobenzene (equation g above) would compete with the reduction process to produce some azoxybenzene (31). Also in the presence of base, N-phenylhydroxylamine undergoes mutual oxidation-reduction to give azoxybenzene (62). This was demonstrated qualitatively, for the addition of N-phenylhydroxylamine to an aqueous solution of sodium sulphide gave an immediate pale-yellow precipitate, presumably azoxybenzene. Moreover, N-phenylhydroxylamine absorbs strongly in the ultra-violet at 320 μ and thus would have been detected when the reaction solutions were examined, as described above, for azoxybenzene.

B. Thiosulphate formation

Bullock and Forbes (9) have established the formation of thiosulphate ion during the course of the reduction of sodium meta-nitrobenzenesulphonate with sodium disulphide in aqueous solution. Similarly Rashevskaya (33) has shown that thiosulphate ion is one of the oxidation products of sulphide ion in the reduction of various substituted nitro compounds by sodium sulphide in aqueous solution. He found that the larger the ratio of sodium sulphide to nitro compounds, the lower was the proportion of

thiosulphate formed, compared to polysulphide. Thus in the reduction of o-nitrophenol, where the initial ratio of sulphide to nitro compound was 0.75:1, practically all the sulphide was oxidized to thiosulphate after two hours at 100°C, very little polysulphide remaining. However, if the initial ratio was about 5:1, after six hours at 50°C when over 99% of the nitro compound had been reduced, only about 5% of the original sulphide was converted to thiosulphate. The remainder of the sulphide oxidation was accounted for as polysulphide.

In the procedure of both these groups of workers, a freshly prepared suspension of cadmium carbonate was used as the precipitant for sulphide and polysulphide ions. Although this was apparently satisfactory in aqueous medium, for the present work in aqueous ethanol it was found to be unsuitable. The presence of ethanol appeared to allow the cadmium carbonate to remain suspended (possibly in colloidal form) and prolonged centrifuging failed to bring about its precipitation. In addition, cadmium carbonate does not bring about the precipitation of hydroxyl ions generated during the reaction and indicated in the present work by an increase in pH of the reaction solution. It would appear to be necessary to remove hydroxyl ions before titrating for thiosulphate with iodine, as iodine also reacts rapidly with hydroxyl ion (63) according to the equations:



That this reaction results in the instantaneous decolourization of iodine was qualitatively demonstrated during the course of the

present work. Apparently Rashevskaya and Bullock and Forbes did not take this into consideration. The latter workers were certainly aware that hydroxyl ions were present after precipitation of polysulphide with cadmium carbonate. They state that: "If a test of an early stage of the oxidation which has been treated with cadmium carbonate to remove sulphide ions is titrated with standard acid, it is found that there is a large increase in the hydroxyl-ion concentration. . ." Thus the iodine titer actually represented the sum of the thiosulphate and hydroxyl ion concentrations. In other words, the "apparent" thiosulphate ion concentration was too high (64).

In the present work it was found that using cadmium sulphate or nitrate, complete precipitation of sulphide, polysulphide and hydroxyl ions could be obtained even in ethanolic solution. Unfortunately, when this was carried out in the presence of thiosulphate ion, considerable co-precipitation of thiosulphate took place along with the cadmium sulphide. Test mixtures of thiosulphate, sulphide and hydroxyl ions in known concentrations were treated with cadmium sulphate solution. Iodine titrations on the filtrate indicated that as much as 50% of the thiosulphate ion was co-precipitated. The precipitate was washed successively with cold, hot and boiling water in an attempt to leach out the thiosulphate. This proved to be only partially successful and accounted for about another 25% of the thiosulphate ion.

Despite the foregoing considerations, it was decided to use cadmium sulphate as the precipitating agent for sulphide and polysulphide ions, on test portions of a typical reaction mixture. Such a mixture was 0.160 M in sodium sulphide and 0.015 M in

nitrobenzene. Sufficient sulphur was dissolved in this to convert about five per cent of the sodium sulphide to polysulphide in order to eliminate the induction period. After 150 minutes at 50°C an aliquot of the reaction mixture was treated with cadmium sulphate and the filtrate titrated with standard iodine solution. A thiosulphate concentration of about 0.002 M was indicated. When the same procedure was carried out after only 10 minutes of reaction, the increase in thiosulphate ion concentration was apparently ca. 0.0002 M. Thus a definite increase in thiosulphate ion could be observed, despite the loss in thiosulphate ion due to coprecipitation which was presumably taking place. However, it is evident that this procedure was unsatisfactory for exact determinations of thiosulphate ion concentrations during the course of a reduction. It did serve nevertheless to qualitatively demonstrate the formation of thiosulphate in these reductions.

In order to illustrate this further, it was decided to use cadmium carbonate as a precipitant and to subsequently remove the ethanol by distillation. The procedure employed is described in detail in the Experimental section. Titration of the final filtrate with standard iodine indicated a thiosulphate ion concentration of 0.004 M. This procedure would be quite inconvenient for repeated thiosulphate determinations and, as previously pointed out, does not take into account the failure of cadmium carbonate to precipitate hydroxyl ions. However, it did serve to demonstrate the formation in these reductions of some species which reduced iodine, but which was not precipitated by cadmium ion. This species was presumably thiosulphate. Although thiosulphate formation has been demonstrated in aqueous solution for the sodium sulphide reduction of

various substituted nitrobenzenes by Rashevskaya, it does not appear to have been done for nitrobenzene itself in aqueous ethanolic solution. The final concentration of 0.004 M thiosulphate ion found in this work relative to the initial concentration of sulphide ion used, is of the same order as that found by Rashevskaya under similar conditions in aqueous solutions.

C. Air oxidation of polysulphide solutions

As pointed out above, the polysulphide solutions encountered in this work are highly susceptible to air oxidation (65). At low dissolved sulphur concentrations, even the air dissolved in the solvent is responsible for a significant proportion of this oxidation. For example, 100 ml of 0.160 M sodium sulphide in the aqueous ethanol was prepared in which sufficient sulphur had been dissolved to make the solution 0.0016 M in sodium disulphide. On standing overnight in a tightly stoppered 100 ml Erlenmeyer flask at 0°C, the yellow colour of the solution was found to be completely discharged.

It was qualitatively established that the result of this air oxidation of polysulphide was thiosulphate ion. Air was bubbled through a 0.160 M solution of sodium sulphide in which sulphur had been dissolved to make the solution 0.0160 M in sodium disulphide. After about two hours the yellow colour of the solution was discharged. Excess cadmium sulphate was then added to precipitate sulphide ion, and the solution filtered. Acidification of a test portion of the resultant colourless filtrate produced a heavy white sulphur precipitate, after a few seconds delay, characteristic of thiosulphate. This was accompanied by the odour of sulphur dioxide. Other test portions of the solutions discharged

the colour of iodine and turned an acidified potassium dichromate solution green. No precipitate was observed on treating a test portion of the solution with cadmium or mercuric ion, eliminating the possibility of sulphide ion remaining in solution. The original sodium sulphide solution, after treatment with excess cadmium sulphate, removal of the precipitate by filtration and acidification of the filtrate, gave only a slight opalescence. This indicated that only a trace of thiosulphate was present in the original sulphide solution (see also Experimental section).

Once precautions had been taken to eliminate all possibility of air oxidation, it was found that the absorbances of polysulphide solutions remained constant over extended periods of time.

SECTION 2.

RESULTS AND DISCUSSIONS

Part III

An Exploratory Study of the Kinetics and Mechanism of the Reduction of Nitrobenzene by Sodium Sulphide in Aqueous Ethanol

A. Method of rate determination

The method devised for following the disappearance of nitrobenzene takes advantage of nitrobenzene's strong absorbance in the ultra-violet with a maximum at $265 \text{ m}\mu$. It was first established that the absorption of nitrobenzene in aqueous ethanol at $265 \text{ m}\mu$ obeyed Beer's law over the concentration ranges studied (see Experimental section Fig. 18, plot I). The procedure described in the experimental section involves measuring the absorbance of a suitably diluted and acidified aliquot sample of the reaction mixture. It was necessary, therefore, to ascertain what species were present in the reaction mixture and, if necessary, to make allowance for any interfering absorbances due to species other than nitrobenzene present.

As seen from the results reported above in Section 2, Part II, the only organic species present in significant concentration at any given time are nitrobenzene and aniline. Although aniline does absorb at $265 \text{ m}\mu$, its hydrochloride absorbs negligibly at this wavelength; hence the solvent used in diluting the aliquot portions of the reaction mixture contained sufficient hydrochloric acid to ensure aniline hydrochloride formation.

Sodium sulphide absorbs at $265 \text{ m}\mu$ after acidification, but

only to a small extent. This is presumably due to the hydrogen sulphide, as sodium chloride solutions of comparable strength have a negligible absorbance. Fortunately the concentration of the interfering species remained fairly constant during the reduction, and, thus, a constant value of 0.015 was subtracted from all absorbance measurements to allow for this. On the other hand, acidified polysulphide absorbs quite strongly in the ultraviolet (20); and, as its concentration was continually changing, it was important that suitable allowance be made for its interference at $265 \text{ m}\mu$.

Ogata et al. used a similar spectrophotometric method for following the reduction of nitrobenzene by sodium disulphide (10). Allowance was made for interfering species by taking the difference of the absorbances at $270 \text{ m}\mu$ (a maximum) and $245 \text{ m}\mu$ (a minimum) as a measure of nitrobenzene concentration. This commonly used procedure implicitly assumes that the absorbance of interfering species is the same at both wavelengths. However, the present study has shown that the absorbances of polysulphide solutions after dilution and acidification are appreciably different at $265 \text{ m}\mu$ and $240 \text{ m}\mu$. This is illustrated in the following table for different concentrations of sodium disulphide:

<u>Absorption at $265 \text{ m}\mu$</u>	<u>Absorption at $240 \text{ m}\mu$</u>
0.098	0.125
0.213	0.260
0.361	0.412
0.510	0.580

It was assumed accordingly that the interfering absorbance at $265 \text{ m}\mu$ was due to dissolved sulphur. However, it was found possible to relate absorbance measurements of disulphide solutions

in the visible ($450 \text{ m}\mu$) with those at $265 \text{ m}\mu$ after dilution and acidification (see Experimental). Thus it was possible to determine the interference due to disulphide, at $265 \text{ m}\mu$ in each case.

B. The effect of added sulphur on the rate of reduction of nitrobenzene by sodium sulphide in aqueous ethanol

On the assumption that a 10-fold excess of sodium sulphide over nitrobenzene would give a pseudo first order reaction, data for the disappearance of nitrobenzene with time were obtained for the reaction of 0.0150 M nitrobenzene with 0.160 M sodium sulphide in aqueous ethanol (approximately 61:39 water: alcohol, by weight) at 50°C , carefully protected by an atmosphere of nitrogen. The data is shown conveniently in Fig. 2, plot I. The existence of an induction period and an autocatalytic reaction is clearly shown here and is in agreement with the previously mentioned work of Bullock and Forbes (9) on sulphide reduction of nitro compounds in aqueous solution. They discovered that, of the reaction products, only polysulphide was responsible for the autocatalytic reaction. This has been supported in the present study by the observation that replacement of some of the sodium sulphide by disulphide shortened or practically eliminated the induction time (Fig 2, plots II-IV). When 2% of the sodium sulphide was present as disulphide, the induction period was reduced to about 25 minutes, while a molarity of added elemental sulphur greater than 0.0075 (4.7%) gave a reaction practically devoid of an induction period.

Corroboration that the reactive species is, in fact, an increasing quantity of polysulphide was found by simultaneously following the change in polysulphide concentration during the

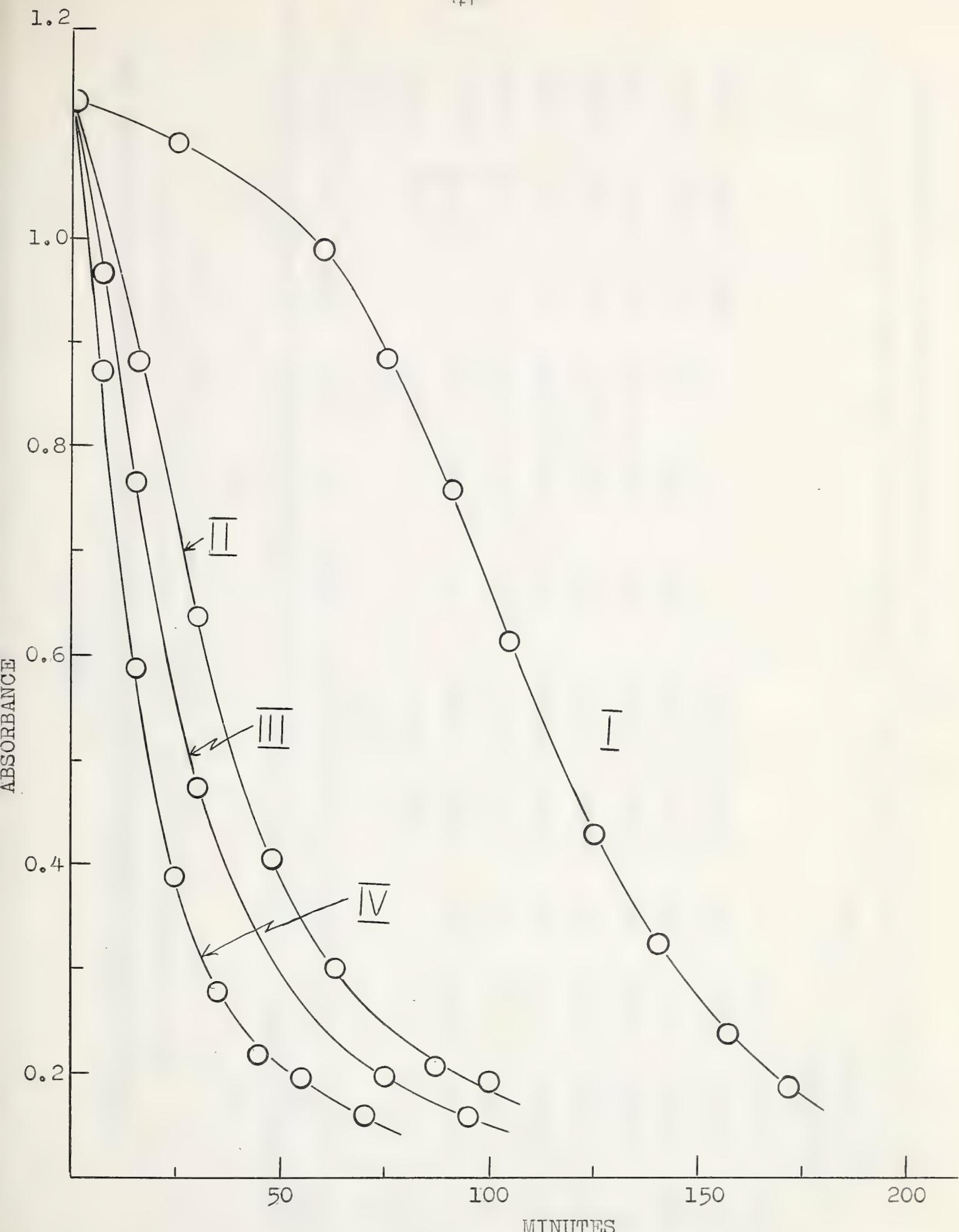


Fig. 2. The change in absorbance of nitrobenzene at $265\text{ m}\mu$ with time during the reduction at 50°C of 0.015 M nitrobenzene by aqueous ethanolic sodium sulphide (details overleaf).

TABLE 2

Effect of Added Sulphur on The Rate of Reduction of Nitrobenzene by Sulphide Ion

Data plotted in Fig. 2. Initial concentrations of nitrobenzene and sulphide ion, 0.0150 M and 0.160 M respectively.

Time*	A**	Ac***	No added sulphur		5% added sulphur		10% added sulphur		20% added sulphur	
			Time	A	Time	A	Time	A	Time	A
0	1.131	0		1.133	0		1.130	0		1.130
25	1.113	1.090	8	1.106	0.990	7	1.150	0.965	7	1.142
61	1.015	0.968	15	1.015	0.880	15	0.970	0.764	15	0.900
75	0.940	0.882	30	0.790	0.634	30	0.690	0.471	25	0.700
91	0.830	0.757	48	0.568	0.404	58	0.440	0.207	35	0.582
105	0.695	0.611	63	0.460	0.300	75	0.385	0.194	46	0.504
125	0.524	0.428	82	0.360	0.205	95	0.337	0.158	55	0.475
140	0.425	0.322	100	0.340	0.193	120	0.302	0.132	70	0.425
157	0.345	0.238	131	0.268	0.135				100	0.387
172	0.295	0.186								0.136

* in minutes

** absorbance at 265 m μ

*** absorbance at 265 m μ corrected for interfering sulphur (see Experimental)

**** initial absorbances in each case calculated from known nitrobenzene concentrations

course of the reduction. Polysulphide absorbs quite strongly over a broad region but is quite measurable at $450 \text{ m}\mu$. In a plot of concentration of sulphur as polysulphide in 0.160 M sodium sulphide in aqueous ethanol versus absorption at $450 \text{ m}\mu$ at 25°C and 50°C , it was found that Beer's law held remarkably well even up to a molarity of 0.08 for elemental sulphur (see Experimental section Fig. 19.).

From Fig. 3, plot I, it is seen that in the reaction between sodium sulphide and nitrobenzene, the disulphide concentration increased to a maximum at about 175 minutes of reaction, slowly decreasing thereafter. This value became constant when the reduction had been completed, a fact not shown in the plot but actually determined in two separate cases. When sulphur was added initially, not only was the rate of increase of disulphide greater with larger initial concentration of disulphide, but so was the rate of loss of disulphide.

C. The Effect of Addition of Base on the Reduction of Nitrobenzene by Sodium Sulphide

The addition of sodium hydroxide increased the rate of reduction of nitrobenzene by sulphide as shown in Fig. 4. Firstly, the effect of adding a one molar equivalent of sodium hydroxide to the sodium sulphide solution was studied. The results appear in Fig. 4, plot II. Subsequent addition of base increased the rate further, but not in proportion to the amount of base added, (Fig. 4, plots III and IV). Eventually a state was reached (1.600 M sodium hydroxide) where further addition of base actually caused a decrease in rate compared with that observed at the next lower base concentration of 0.800 M sodium hydroxide. This is illustrated

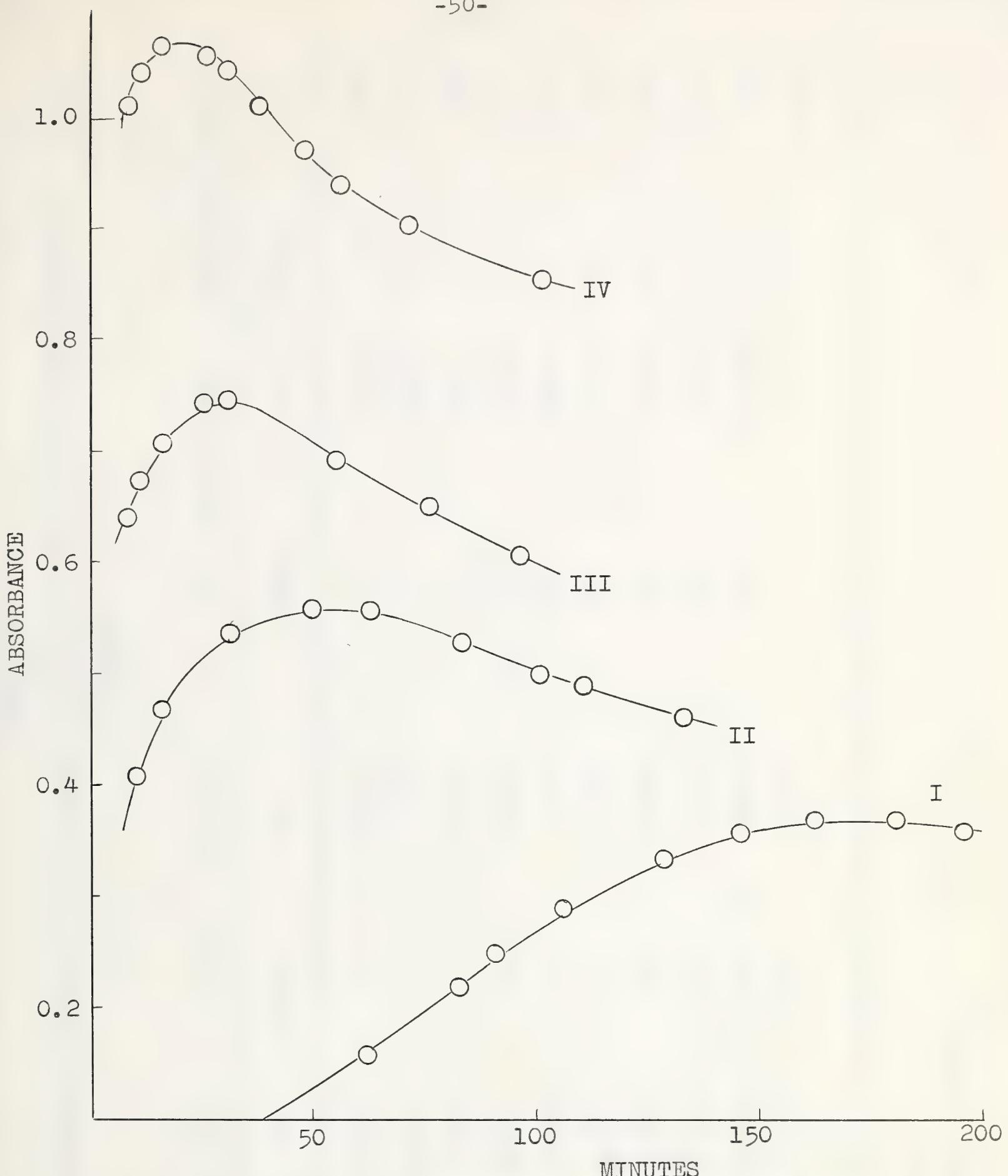


Fig. 3. The change in absorbance at $450\text{m}\mu$ with time during the reduction of 0.0150 M nitrobenzene in aqueous ethanolic sodium sulphide. I to IV have a Na_2S concentration of 0.160 M. In addition II, III and IV are 0.0075 M, 0.015 M and 0.030 M respectively in dissolved sulphur.

TABLE 3

Corresponding Changes in Absorbance at 450 m μ for the Reductions Recorded

in TABLE 2

I		II		III		IV	
Time*	A**	Time	A	Time	A	Time	A
no added sulphur	0.085	2	0.235	8	0.780	8	1.235
55	0.175	9	0.495	11	0.820	11	1.272
62	0.192	16	0.570	16	0.861	16	1.300
82	0.265	31	0.650	25	0.905	26	1.220
92	0.302	49	0.680	31	0.910	30	1.275
106	0.350	64	0.675	59	0.841	57	1.255
128	0.402	83	0.640	76	0.792	77	1.155
146	0.436	101	0.610	96	0.742	56	1.145
162	0.450	110	0.598	121	0.702	71	1.100
180	0.450	132	0.561	101	1.010		

* in minutes

** absorbance at 450 m μ

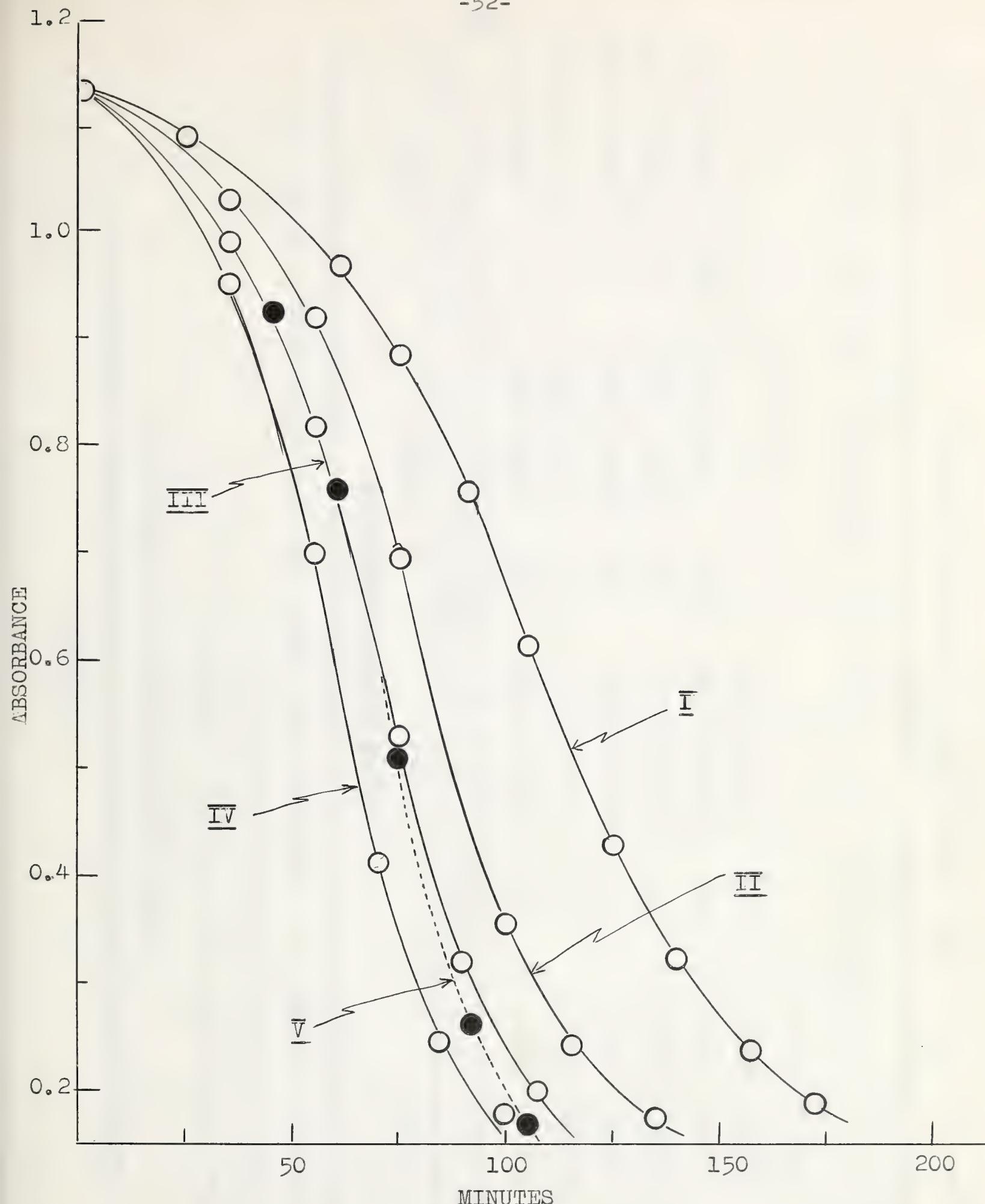


Fig. 4. Absorbance at 265 m μ vs. time during the reduction of 0.015 M nitrobenzene in aqueous ethanol at 50°C by 0.160 M Na₂S. I contains no added NaOH, and II, III, IV and V are 0.16 M, 0.32 M, 0.80 M and 1.60 M in NaOH respectively.

TABLE 4

Effect of Added Base on the Rate of Reduction (Change in Absorbance at 265 m μ) of Nitrobenzene by Sulphide Ion

Initial nitrobenzene concentration, 0.0150 M.

Initial sulphide ion concentration, 0.160 M.

Data plotted in Fig. 4 (data for plot I being the same as for plot I in Fig. 2).

Minutes	Sodium Hydroxide Molarity						Minutes	A*	A ^{**}	A ^{***}	A ^{****}	A ^{*****}
	0.160	0.320	0.800	1.60	53-							
35	1.058	1.030	35	1.024	0.991	35	0.982	0.951	45	0.950	0.925	
55	0.960	0.920	55	0.868	0.817	55	0.750	0.700	60	0.795	0.760	
75	0.755	0.694	75	0.618	0.530	70	0.487	0.411	75	0.565	0.511	
100	0.450	0.355	90	0.421	0.319	85	0.355	0.243	92	0.355	0.260	
115	0.394	0.240	108	0.320	0.198	100	0.306	0.176	105	0.282	0.164	
135	0.292	0.172	130	0.287	0.162							
160	0.245	0.125										

* Observed absorbance at 265 m μ . ** absorbance at 265 m μ corrected for interfering sulphur (see Experimental Section for typical calculation).

by plots IV and V in Fig. 4.

The increased rate was no doubt due to the conversion of the relatively unreactive HS_2^- to the much more reactive species, S_2^- . A large concentration of base would convert essentially all the polysulphide to the unhydrolyzed state and result in a maximum rate of reduction. However, the increased concentration of base caused greater reaction between hydroxyl ion and the "active sulphur" (9), hence less disulphide was formed, thus leading to a lower acceleration of rate. With sufficiently high concentration of base it is expected that most if not all of the active sulphur would be lost as thiosulphate, and no autocatalysis would be observed. This could not be tested in this work since a concentration of base significantly greater than 4 M resulted in a salting-out of the ethanol.

The changes in "polysulphide concentration" accompanying the reductions in each of these cases are shown in Fig. 5. The absorption shown in Fig. 5 must be a composite of increased polysulphide concentration as a result of reduction, and a larger ratio of disulphide to hydrodisulphide ion, the magnitude of which depends upon the hydroxyl ion concentration. Hence, calculation of the polysulphide sulphur from these absorption measurements, using the calibration data from the Beer's law plot would give erroneous results. With the aid of Fig. 1, the absorbances at various base concentrations have been converted to those where no base was added, and thus it was possible to show the real increase of polysulphide sulphur which occurred during these reductions in basified solutions. Fig. 6 shows clearly the diminishing increase of polysulphide sulphur as the

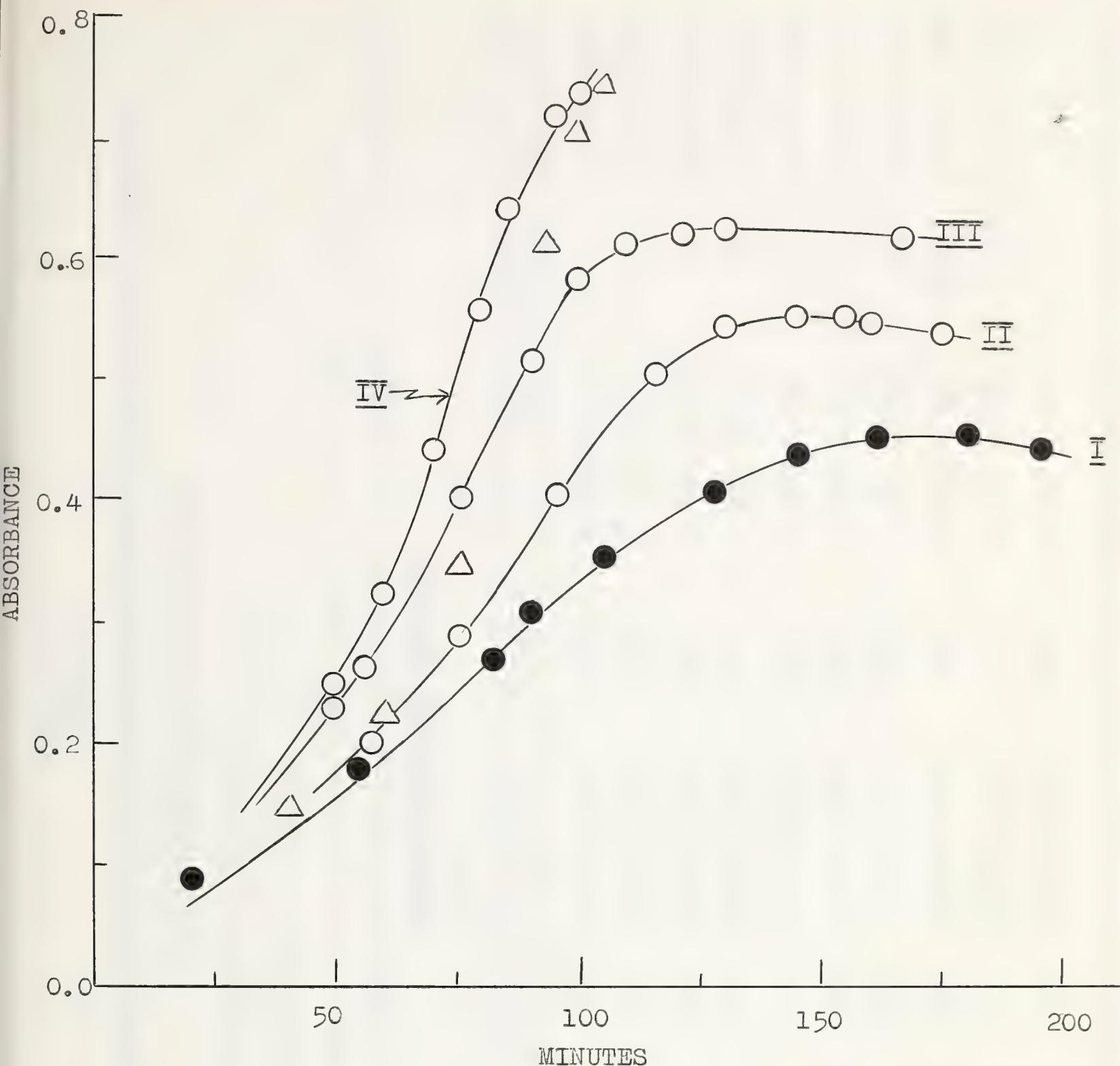


Fig. 5. The absorbance at 450 m μ vs. time during the reduction of 0.015 M nitrobenzene in aqueous ethanol at 50°C by 0.160 M Na₂S. I contains no added NaOH, and II, III, IV, and V (Δ) are 0.16 M, 0.32 M, 0.80 M and 1.60 M in NaOH respectively.

TABLE 5

Effect of Added Base on the Rate of Reduction (Change in Absorbance at 450 m μ)

of Nitrobenzene by Sulphide Ion

Initial nitrobenzene concentration, 0.0150 M.

Initial sulphide ion concentration, 0.160 M.

Data plotted in Fig. 5 (the data for plot I being the same as for plot I in Fig. 3).

Sodium Hydroxide Molarity							1.60	
Minutes	A*	Ac**	Minutes	A*	Ac**	Minutes	A*	Ac**
0.160	0.117	0.106	30	0.147	0.122	30	0.158	0.117
57	0.286	0.260	50	0.225	0.187	36	0.175	0.130
76	0.286	0.260	56	0.260	0.216	50	0.245	0.181
96	0.401	0.365	76	0.400	0.333	56	0.287	0.213
116	0.500	0.455	91	0.512	0.427	66	0.380	0.281
130	0.540	0.491	100	0.582	0.486	71	0.439	0.325
146	0.550	0.500	109	0.610	0.509	80	0.555	0.411
155	0.548	0.498	122	0.620	0.517	86	0.638	0.472
161	0.544	0.494	131	0.623	0.519	95	0.715	0.530
175	0.535	0.486	167	0.615	0.512	101	0.735	0.545

* Absorbance at 450 m μ . ** Absorbance at 450 m μ corrected for base (see Experiment 5) - plotted in Fig. 6.

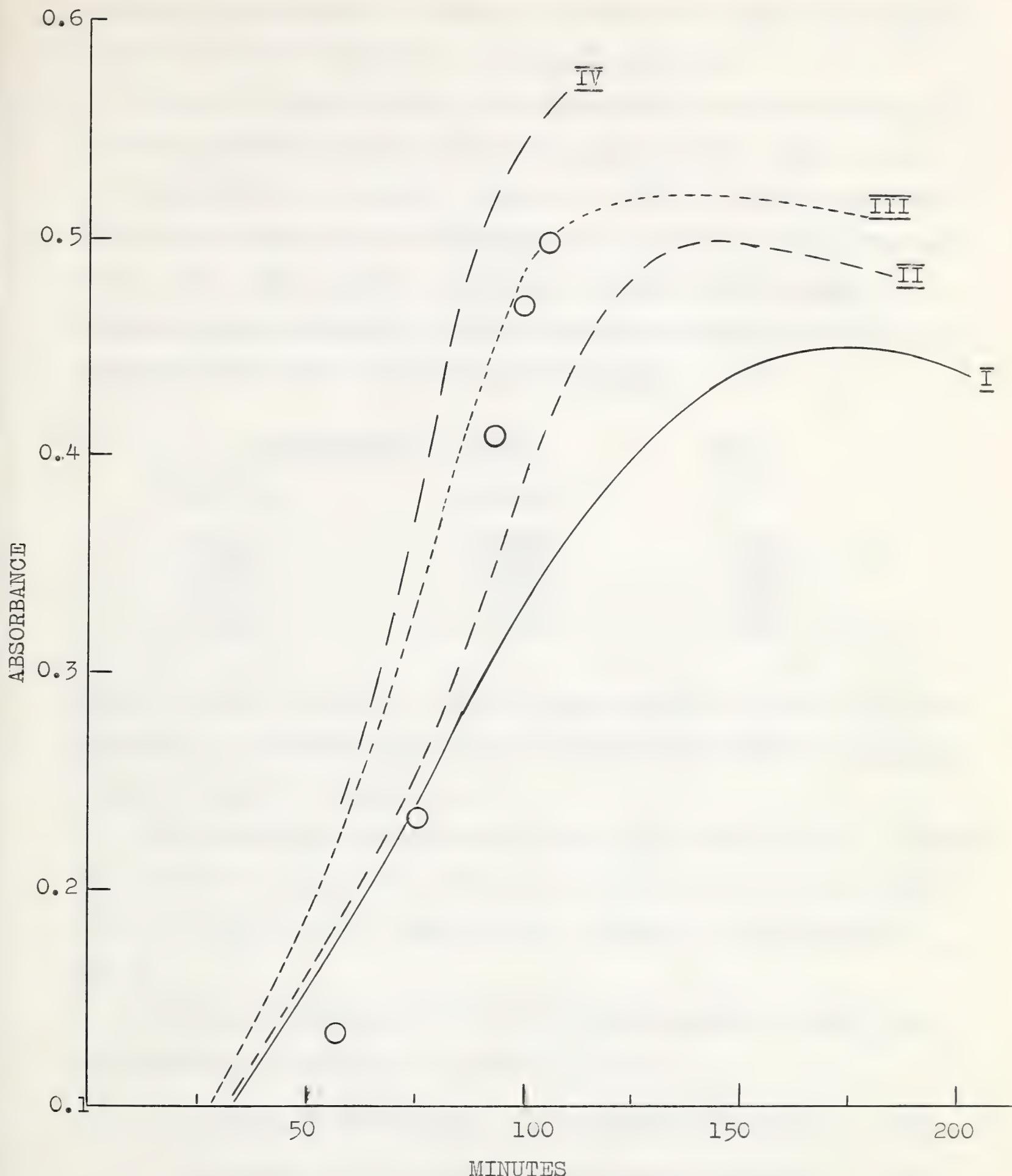


Fig. 6. The corresponding absorbances at 450 m μ from Fig. 5 corrected for the effect of increased OH⁻ ion concentration on the absorbance at 450 m μ . (here O represents 1.60 M NaOH)

initial concentration of base is increased and thus, the greater extent of loss of sulphur by reaction with base.

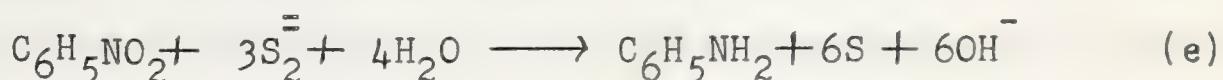
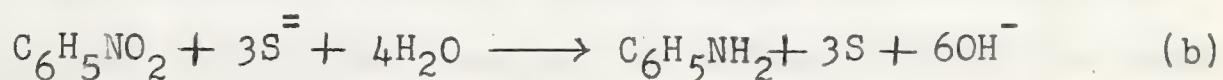
Figure 1 was obtained by the progressive basification of a sodium sulphide solution containing one specific concentration of polysulphide, and gave a figure of 1.80 for the ratio of absorbance of basified (4M) solution to that of the unbasified solution. The same figure of 1.80 was obtained when a number of solutions were prepared, differing only in concentration of polysulphide, and made 4 M in sodium hydroxide.

	<u>Absorbance at 450 mμ</u>	<u>Ratio</u>
unbasified	basified	
0.117	0.206	1.81
0.165	0.286	1.80
0.375	0.675	1.82
0.540	0.968	1.79
0.735	1.315	1.79

Hence the use of Fig. 1, and the ratios implied therein, for the conversion of absorbances of the basified polysulphide solutions shown in Fig. 6 is justified.

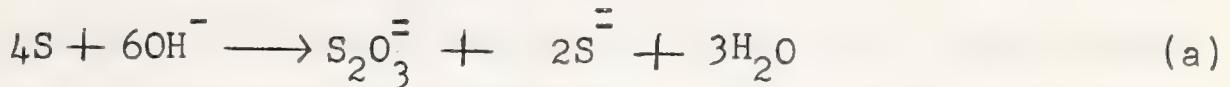
The foregoing considerations raise the question as to whether the increase in pH, which takes place during reduction, is partially responsible for the observed increase in absorbance at 450 m μ .

During a reduction of 0.0150 M nitrobenzene, hydroxyl ions are generated according to equation b and e:



At half life, based on nitrobenzene concentration, the concentration

of hydroxyl ions generated should be 0.045 M. Actually, it will be less than this because of the intercedence of the reaction denoted by equation a.



Referring to Fig. 1 this represents an increase in absorbance of less than 0.020, which corresponds to maximum error of less than 2%. Hence the increase in pH observed during the reduction can be considered as having a negligible effect on the absorbance at 450 m μ .

D. The Induction Period

The initially slow reaction between sodium sulphide and nitrobenzene (Fig. 2, plot 1) might be attributed to one, or a combination, of the species present as a result of hydrolysis of sodium sulphide. These are principally the sulphide and hydrosulphide ions, with possibly small concentrations of disulphide and hydrodisulphide ions as contaminants. It was originally thought that the slow reaction was due largely, if not completely, to the small concentration of contaminating disulphide ion. Support for this view was obtained by the observation that this initial rate was found occasionally to be considerably greater (twice or three times) than that usually observed, depending upon the source (and hence extent of contamination by $S_2^{\cdot-}$) of the sodium sulphide. This increase in the initial rate could hardly be attributed to a significant change in the monosulphide ion concentration due to hydrolysis, since the concentration of 0.160 M in sodium sulphide was adhered to as closely as possible. The species which could change sufficiently in concentration to effect

this two or three-fold increase in initial rate was more reasonably the contaminating, much more reactive, disulphide ions. However because of the reasons indicated below, it is probable that the initial slow reduction is at least to a large extent due to sulphide and hydrosulphide ions. It would be expected that of these two ions ($S^=$ and SH^-) the protonated sulphide ion should release electrons less readily than the unprotonated sulphide ion, in view of the larger, more diffuse, electron cloud of the latter. In other words the sulphide ion should be the stronger reducing agent of the two.

A preliminary study of the sodium hydrosulphide reduction of nitrobenzene indicated that the initial rate of reduction was slower than that in the sodium sulphide reduction, (see next section Fig.7 plot II). The sodium hydrosulphide was prepared in this instance by adding the requisite amount of hydrochloric acid to sodium sulphide. No attempt was made to allow for the interfering absorbance, due to the small amount of polysulphide formed during the course of the first 200 minutes of the reduction. However, the initial rates indicate that sulphide reduces two to three times faster than hydrosulphide. Allowing that in solution, the sulphide is approximately 40% hydrolyzed to the hydrosulphide, the sulphide ion apparently reduces in the order of five times more quickly than the hydrosulphide ion. Although the reducing ability of the hydrosulphide ion is lower than that of sulphide, it is sufficiently high to make a significant contribution to the overall initial rate.

The extremely slow reduction by the sulphide ion might be due to the fact that it is much more strongly hydrated than is

the hydrosulphide ion (14). The displacement of the water to allow association of the sulphide ion with the nitro group for the subsequent electron transfer occurs with difficulty. In contrast, disulphide and polysulphide ions reduce nitrobenzene much more rapidly, no doubt due in part to the lower degree of hydration of these ions (17). Furthermore, it is not unreasonable to assume that the conversion $\overset{\cdot}{\text{S}}\cdot\overset{\cdot}{\text{S}}\cdot\overset{\cdot\cdot}{\text{S}}\cdot\overset{=\cdot}{\text{S}}\cdot\rightarrow 2\text{e} + \overset{\cdot}{\text{S}}\cdot\overset{\cdot}{\text{S}}\cdot\overset{\cdot\cdot}{\text{S}}\cdot$ is more facile than is the analogous change of $\overset{\cdot\cdot}{\text{S}}\cdot\overset{=\cdot}{\text{S}}\cdot\rightarrow 2\text{e} + \overset{\cdot}{\text{S}}\cdot$ on the basis that the combination of the two sulphur atoms yields a more stable product.

E. The Autocatalytic Reaction

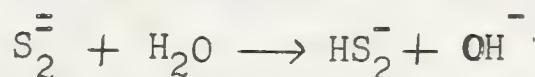
The effective reducing species has been shown to be the disulphide ion. Since this is present in a concentration less than or comparable to that of the nitrobenzene, although increasing as the reaction progresses, it is obvious that a pseudo first order reaction cannot be obtained. The data shown in Fig. 2 indicates that the reduction is autocatalytic in nature.

If the relatively small contribution of the monosulphide and hydrosulphide to the rate can be ignored, it might be possible to apply the general equation for autocatalytic reactions to the disulphide reduction of the nitrobenzene (66). Although the concentration of nitrobenzene can be accurately determined at any time by absorption measurements, the problem of determining disulphide concentration is a much more complex one. The concentration of disulphide ion during the course of the reduction is governed by several factors. Firstly, it is generated as a result of the interaction of sulphide ion and sulphur (equation c, page 14) the latter arising from the reduction

processes represented by equations b, j and e (pages 13, 22 and 53 respectively). Disulphide ion is therefore removed from the system indirectly only via the reaction of sulphur with hydroxyl ions, as indicated in equation a (page 13). In addition, at any time the concentration of disulphide ion will be dependent on the pH of the solution; and, as might be anticipated from the equations representing the reduction process (b, j and e), the pH increases during the reduction. In a typical reduction, the pH, which was initially 12.60, rose to a maximum of 12.95 after 45 minutes of reaction. After 130 minutes, well beyond one-half life, a pH of 12.50 was observed. All pH measurements in this example were made at 50°C.

Under these circumstances, a fairly accurate value for the hydrolysis constant of the disulphide ion is required in order to ascertain the concentration of disulphide ion. The lack of any useful literature value, particularly for 50°C and for aqueous ethanol, led to the unsuccessful attempt described herein to evolve a spectrophotometric method for determining the extent of hydrolysis of disulphide ion under the conditions of this reduction (p. 30).

According to Fig. 1 showing the relationship between absorbance and hydroxyl ion concentration, it is very probable that the pH changes occurring during the reduction and recorded above, involve only small changes in the hydrolysis equilibrium.



F. Summary of the course of reduction of nitrobenzene by sodium sulphide in aqueous ethanol

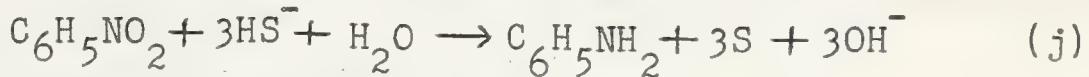
Any explanation of the course of this reduction must take

into account all the observations previously mentioned and now summarized below for convenience. Thus, the account must take into consideration:

1. The extent of hydrolysis of sodium sulphide in aqueous ethanol (i.e. about 40%).
2. The induction period, which was practically eliminated by conversion of about 5% of the sulphide present to disulphide.
3. That in all cases the polysulphide concentration increased to a maximum and then declined to some constant value.
4. The autocatalytic nature of the reaction as observed in the plot of nitrobenzene absorbance vs. time (Fig. 2)
5. The formation of thiosulphate ion.
6. The increase to a maximum and subsequent decrease of the pH during the reduction.

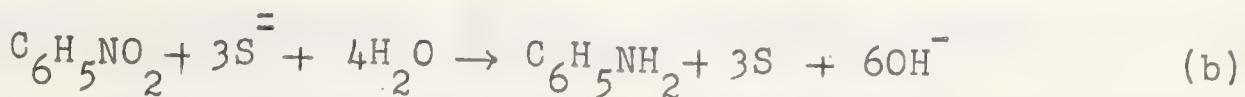
The information obtained from the foregoing experiments and discussion has thus led to the following account of a possible course of reduction of nitrobenzene by sodium sulphide.

At the beginning of the reaction the only reducing species present are sulphide and hydrosulphide ions in approximately equal concentration. Hydrosulphide ion reduces the nitrobenzene very slowly according to equation ¹j to give sulphur.



1. However as will be shown in the next part of this section, in the absence of a stronger reducing agent such as sulphide and polysulphide, this stage of the reaction initially goes only as far as N-phenylhydroxylamine formation, the final stage of reduction to aniline taking place much more slowly.

In a similar manner sulphide ion also reduces the nitro-benzene but about five times faster than does the hydrosulphide ion.



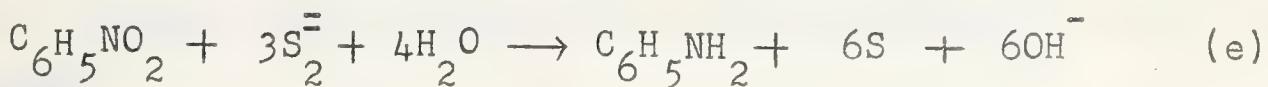
The sulphur formed from reactions b and j reacts very quickly (no precipitation of sulphur ever occurs under the conditions of these reductions) with either sulphide to give polysulphide ion (equation c).



or with hydroxyl ion to give thiosulphate according to equation a



The polysulphide produced via equation c is responsible for the increase in absorbance at $450\text{m}\mu$ and reduces the nitro compound much more quickly than do either sulphide or hydrosulphide ions.



The sulphur formed from reaction e also reacts via equations c and a to give more polysulphide and thiosulphate ion. The formation of polysulphide and its superior reducing ability accounts for the autocatalytic nature of this reaction and the exponential increase in polysulphide concentration.

If there were no competition from hydroxyl ions for the sulphur initially formed, the polysulphide concentration would be expected to increase rapidly, and asymptotically reach a maximum value. However the competitive reaction with hydroxyl ions is

quite significant and becomes more important as the sulphide and hydrosulphide ion concentrations decrease.

The hydroxyl ion concentration increasing via the reactions indicated by equations b, e and j, eventually reaches the stage where it competitively removes the sulphur as fast as it is generated by reaction c. This point corresponds to the maximum absorbance at $450 \text{ m}\mu$ (due to polysulphide) reached in all these reductions. Subsequently the reaction of sulphur with hydroxyl ions is the predominating one and there is a decline in polysulphide concentration, accompanied by a decrease in hydroxyl ion concentration. However, polysulphide does not disappear due to direct reaction of the polysulphide with base, but is removed only by reaction of base with the "active sulphur", produced during the course of reduction. Thus when the reduction process is practically complete, the formation of thiosulphate ceases and the polysulphide concentration remains constant. This was demonstrated in at least two instances where absorbance measurements were made at $450\text{m}\mu$ over a 24 hour period and no change in absorbance observed.

Although the polysulphide formed in these reductions has been indicated as being unprotonated, it is likely that to some extent it is hydrolyzed. However, the degree of hydrolysis should be lower than for sulphide ion. The resulting hydrosulphide, according to the results obtained in the next part of this section, reduces nitrobenzene only slightly faster than does hydrosulphide ion and about as fast as does the sulphide ion. Thus a total of four different reducing species contribute to the overall rate of reduction, but with the disulphide (polysulphide) ion making by far the greatest contribution.

SECTION 2

RESULTS AND DISCUSSIONS

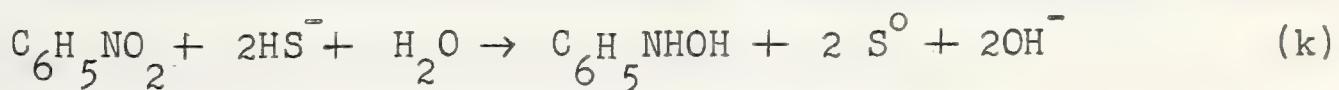
Part IV

The Products of the Reduction of Nitrobenzene by Sodium Hydro- sulphide in Aqueous Solution

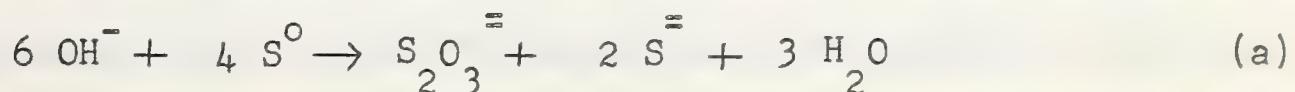
A. The reaction conditions

It was found in a preliminary study of the reduction of nitrobenzene by sodium hydrosulphide in aqueous ethanol (see part V of this section) that the rate of the reduction was too slow to study conveniently in any detail. Thus it was decided to study the reduction in aqueous solution where the reaction took place much more quickly. Ogata et al (10) had also observed that with sodium disulphide reductions of nitrobenzene the rate of reaction increased with increasing content of water in the solvent. However the use of water as a solvent limited the nitrobenzene concentrations used in this work to 0.015 M or less.

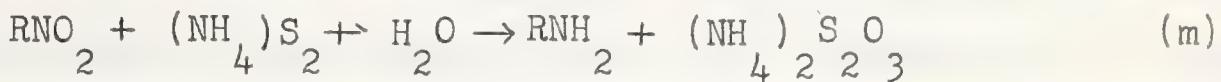
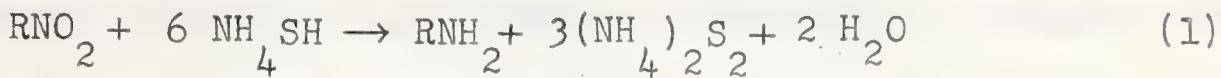
Normally reductions by hydrosulphide ion involve an increase in pH due to the formation of hydroxyl ions according to equation k.



This in turn gives rise to reaction a in which elemental sulphur is considered to be lost by conversion to sulphide and thiosulphate ions.



In his review of methods of reduction of nitro compounds Schröter (13) suggests that in the case of ammonium hydrosulphide reduction, thiosulphate formation occurs directly as result of the two reactions 1 and m.



However it is likely that the thiosulphate arises indirectly through a reaction such as a (9). If that is so then by keeping the hydroxyl ion concentration low relative to the hydrosulphide ion concentration, it should be possible to minimize or eliminate the formation of thiosulphate ion thus retaining the elemental sulphur either as S^0 or as HS_x^- as has been done by Bullock and Forbes (9) for sulphide and disulphide reductions of nitro compounds. To this end, the sodium hydrosulphide solution used in this work was prepared by adding slightly more than a molar equivalent of ammonium chloride to an aqueous sodium sulphide solution (see Experimental section). Although the pH of the reaction solution increased only slightly (9.0 to a maximum of 9.4, at 50°C) during the course of the reaction, the attempt to eliminate thiosulphate by this method was unsuccessful.

The procedures and experimental conditions adopted are recorded in detail in the Experimental section.

B. Organic products of the reduction of nitrobenzene and of phenyhydroxylamine by hydrosulphide and hydrodisulphide ions

The results reported in Part II A of this section definitely established that the only organic reduction product of nitrobenzene by sodium sulphide or sodium disulphide was aniline.

Since Goldschmidt and Larsen (52) had obtained N-phenylhydroxylamine as the principal product of the reduction of nitrobenzene by sodium hydrosulphide in water at 25°C , it was necessary to determine the products of the present reduction conditions. The analysis of aliquots of the reduction mixtures for organic products by vapor phase chromatography (see experimental) and also by using infrared absorption at 3580 cm^{-1} and 3700 cm^{-1} to detect the presence of phenylhydroxylamine, is summarized in Table 7. As phenylhydroxylamine was definitely shown to accumulate during the course of the reaction, it was necessary to examine the reduction of N-phenylhydroxylamine by hydrosulphide and hydrodisulphide ions. This was carried out employing exactly the same reaction conditions as for the nitrobenzene reductions, except that initial concentrations of 0.010 M phenylhydroxylamine were used. The results of these reductions are also included in Table 7.

Table 7. Products obtained during the reduction of nitrobenzene or N-phenylhydroxylamine by sodium hydrosulphide or sodium hydrosulphide in aqueous media at 50°C.

Initial reducible material (molarity)	Reducing agent (molarity)	Time of reduction	Products of reduction		
			phenylhydroxylamine	Aniline	Unchanged nitrobenzene
Nitrobenzene (0.010)	NaHS (0.150)	60 min.	25%	ca 1%	75%
		3 hours	45%	20%	35%
		18 hours	None	practically all aniline	trace
Phenylhydroxyl amine (0.010)	NaHS (0.150)	50 min.	unchanged	none	-
		90 min.	unchanged	none	-
		24 hours	considerably decreased	much aniline	-
		48 hours	small amount	mostly aniline	-
Phenylhydroxyl amine (0.010)	NaHS (0.150) containing 8% sulphur as HS_2	70 min.	60%	40%	-
		1000 min.	10%	90%	-

The results (Table 7) show clearly that hydrosulphide reduced phenylhydroxylamine extremely slowly, requiring 48 hours for near-completion of the reaction. No reduction apparently occurred for the first 90 minutes. On the other hand hydrosulphide with 8% of the hydrosulphide as hydrodisulphide reduced phenylhydroxylamine to the amine essentially completely in 1200 minutes. In both cases no hydrodisulphide accumulated. Instead the hydrodisulphide originally present was converted to a colourless species, most likely thiosulphate, since thiosulphate was found to increase during the reduction (see Part IV C).

At the beginning of the reaction between nitrobenzene and hydrosulphide, only the hydroxylamine was produced. Further reduction of the phenylhydroxylamine to aniline proceeded much more slowly than did its formation from nitrobenzene, hence phenylhydroxylamine accumulated during the first portion of the reaction. As the reduction of nitrobenzene progressed, hydrodisulphide also accumulated. The hydrodisulphide thus formed reduced phenylhydroxylamine more readily than it reduced nitrobenzene (see Part V of this section). Thus towards the end of the reduction of nitrobenzene by sodium hydrosulphide, the phenylhydroxylamine disappeared, leaving only aniline and some nitrobenzene yet to be reduced.

C. Thiosulphate formation during the reduction of nitrobenzene and N-phenylhydroxylamine by hydrosulphide or hydrodisulphide ion

Thiosulphate determinations were carried out on the reaction solutions by precipitating sulphide and polysulphide with cadmium carbonate and titrating the filtrate with standard iodine solution. The procedure is described at length in the Experimental section. It was also possible from absorption measurements at

450 μ to estimate the concentration of hydrodisulphide at any time during the course of the reaction. The Beer's law plot obtained in Fig. 20 was used to relate absorbance at 450 μ to molarity of hydropolysulphide present, giving an extinction coefficient of 35.0 at 50.0°C for hydrodisulphide ion.

Analysis of a reaction solution, initially 0.010 M in nitrobenzene and 0.150 M in hydrosulphide ion, after 60 minutes revealed a 0.0005 M increase in thiosulphate ion concentration. After 18 hours when the reaction had practically ceased, the thiosulphate ion concentration had increased to 0.0067 M. A similar analysis for the reduction of N-phenylhydroxylamine (0.010 M) by 0.150 M hydrosulphide containing 8% sulphur as hydrodisulphide ion, indicated a net increase in thiosulphate ion concentration of 0.00457 M at reaction completion (1000 minutes). The corresponding change in hydrodisulphide ion concentration during the latter reduction is shown in Fig. 14.

D. Stoichiometry of the overall reduction of nitrobenzene to aniline by sodium hydrosulphide

The quantitative analyses of the initial reaction mixture and of the mixture obtained at the end of the reduction gave the following results.

	<u>Nitrobenzene</u>	$\text{S}_2\text{O}_3^{2-}$	HS^-_2
Initial concentration	0.01 M	0.0035 M	0.0005 M
Final concentration	0.00 M	0.0102 M	0.0035 M
Overall change	0.01 M	0.0067 M	0.0030 M

Thus both $S_2O_3^{2-}$ and HS^- are produced during the reaction and are found at the end of the reduction in the concentration shown.

Assuming that HS^- reduction of nitrobenzene to aniline yields only HS^- one can write the following overall redox equation



On the other hand, the formation of only $S_2O_3^{2-}$ is satisfied by the overall redox equation*



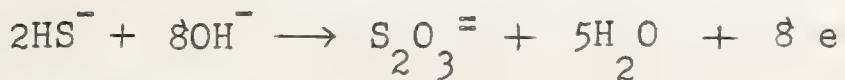
Equation o can be obtained from the following sequence of reactions



given by Bullock and Forbes (9), by a suitable combination of equations j and a, while equation n can be obtained by the combination of j and p. The implication in this is that the reduction of nitrobenzene with consequent production of elemental sulphur and the formation of thiosulphate from this sulphur are two distinct steps in the reaction. The formation of HS^- and $S_2O_3^{2-}$ are then the result of competitive reactions of S^0 with HS^- and OH^- .

*

A combination of the following half-reactions shown below will also give the redox equation o and thus implies a direct formation of thiosulphate from the reduction of nitrobenzene by hydrosulphide.



According to the results of the analyses, tabulated above, either the two reactions n and o occur simultaneously, though to different extents, or the individual reactions shown by equations i, p and a occur and some of the elemental sulphur reacts with the HS^- present rather than with OH^- . It is reasonable to think that elemental sulphur would react more readily with HS^- than with OH^- because of the former's greater nucleophilicity (67) and hence yield a preponderance of HS_2^- rather than $\text{S}_2\text{O}_3^{2-}$. The reverse is apparently true (a possible explanation for this is given in the final summary of the reaction). In the case of Na_2S reduction of nitrobenzene, the sulphide ion, because of its greater charge would compete with OH^- for S° even more effectively and hence a larger proportion of S° produced would be diverted to S_2^- formation rather than $\text{S}_2\text{O}_3^{2-}$ production, as appeared to be the case.

Equation e shows that the production of one mole of HS_2^- required $1/3$ mole of nitrobenzene. Since in this reduction, 0.0030 M of HS_2^- was produced, according to the preceding statement, the amount of nitrobenzene consumed in this direction must have been 0.0010 M . The remainder of the nitrobenzene (0.0090 M) then gave $\text{S}_2\text{O}_3^{2-}$ only. The stoichiometry of equation o shows that 1 mole of nitrobenzene yields $3/4$ mole of $\text{S}_2\text{O}_3^{2-}$. Accordingly, the 0.0090 M of nitrobenzene should yield 0.00675 M of the thiosulphate. The amount actually found (0.0067 M) agrees with this very well and supports the formulations n and o and the concept of a competitive reaction such as indicated in equations p and a.

E. Stoichiometry of the hydrodisulphide reduction of phenylhydroxyl-amine

Quantitative analysis of the initial and final reduction

mixtures yielded the following results.

	phenylhydroxyl amine	$S_2O_3^=$	HS^-_2
Initial concentration	0.010 M	0.0035 M	0.0116 M
Final concentration	0.00 M	0.0080 M	0.0041 M
Overall change	0.01 M	0.0045 M	0.0075 M

Reaction of either HS^- or HS^-_2 with phenylhydroxylamine apparently failed to produce HS^-_2 , but instead consumed any HS^-_2 present. However the amount of $S_2O_3^=$ increased considerably. The following overall redox equation agrees with these results but points out that one mole of phenylhydroxylamine yields 0.5 mole of $S_2O_3^=$.



The formation of 0.0045 mole of $S_2O_3^=$ from the reduction of 0.01 mole of phenylhydroxylamine supports this formulation. The slight decrease from the amount expected theoretically can be attributed to the simultaneous though much slower reduction of the phenylhydroxylamine by the HS^- which is present in a concentration about 10 times that of HS^-_2 . Support for the view that HS^- also participates in the reaction is obtained from the quantitative data indicated above. Since only 0.0075 mole of HS^-_2 was consumed, 0.0025 mole of HS^- must also have reacted to complete the supply of electrons required for the reduction of 0.01 mole of the phenylhydroxylamine to aniline. This gave 0.0025 mole of S^0 which by

equation q must have lead to the production of $\frac{1}{4}$ (0.0025) or 0.0006 mole of $S_2O_3^{2-}$. The amount of $S_2O_3^{2-}$ produced by these two paths then would be $1/2 \times 0.0075 + 0.0006 = 0.0044$ M. The amount of $S_2O_3^{2-}$ actually found (0.0045 M) is in very close agreement with this. Thus the reduction of phenylhydroxylamine by hydrosulphide containing hydrodisulphide also consumes HS^- and thus produces a small amount of the hydrodisulphide. The reaction however shows an overall decrease in hydrodisulphide ion.

SECTION 2

RESULTS AND DISCUSSIONS

Part V

A Study of the Kinetics of the Reduction of Nitrobenzene by
Hydrosulphide Ion in Aqueous Solution

As has already been indicated, a preliminary investigation of this reduction was carried out in aqueous ethanolic solution. It was not found possible to make allowance for interference due to sulphur and thus these results are considered primarily for their qualitative value. Moreover, as it subsequently became evident that N-phenylhydroxylamine was the principal reduction product for at least the first 200 minutes of the reaction, the failure to make allowance for its interference in absorbance measurements at 265μ resulted in a further source of error in this work.

Nevertheless, before considering the results obtained in aqueous solution, it is of some interest to examine briefly the preliminary work carried out in aqueous ethanolic solution.

A. The reduction of nitrobenzene by hydrosulphide ion in aqueous ethanol

In the preliminary examination of this reduction, the sodium hydrosulphide was prepared by adding an equivalent of constant boiling hydrochloric acid to 0.160 M sodium sulphide solution. The reaction was carried out in the 40% by weight ethanol-water mixture, used previously. It was not possible of course, to apply the same corrections for interfering absorbance at 265μ that had been used for the sodium sulphide reduction, viz. Fig. 21. It was

decided, in order to get at least a qualitative estimate of the reducing ability of hydrosulphide ion, to make no allowance for this interference. The error involved in doing this was considered to be small particularly at the beginning of the reduction. Moreover, as the reduction was much slower than the sulphide reduction, the amount of polysulphide generated in a given time is correspondingly small. The change in absorbance at 450 μ in the 200 minute period examined was about 0.10. From a consideration of the relationships in Figs. 19, 20 and 21, this concentration of polysulphide could have accounted only for an interfering absorbance of about 0.015 at 265 μ . The results of a typical reduction are given in Fig. 7 plot II. An initial rate of only 1/2 to 1/3 of that found for the reduction with sodium sulphide was indicated. The marked autocatalytic effect observed in the latter case apparently did not occur in hydrosulphide reduction of nitrobenzene.

The addition of enough sulphur to convert about 10% of the sodium hydrosulphide to the hydrodisulphide gave no apparent increase (Fig. 7 plot III) in the initial rate of this slow reaction. No allowance was made for interfering polysulphide absorbance at 265 μ in this case. It seems likely that if this could have been done, the hydrodisulphide reduction would have been shown to be a slightly faster one than the hydrosulphide reduction. The slow increase in rate shown in Fig. 7 plot II, was at first ascribed to a gradual shift in the equilibrium $S^= + H_2O \rightarrow HS^- + OH^-$ to the left due to the increase in hydroxyl ion concentration resulting from the slow reduction. The observation that pH rose from 10.0 to 10.9 over a period of 630 minutes of reaction supports this

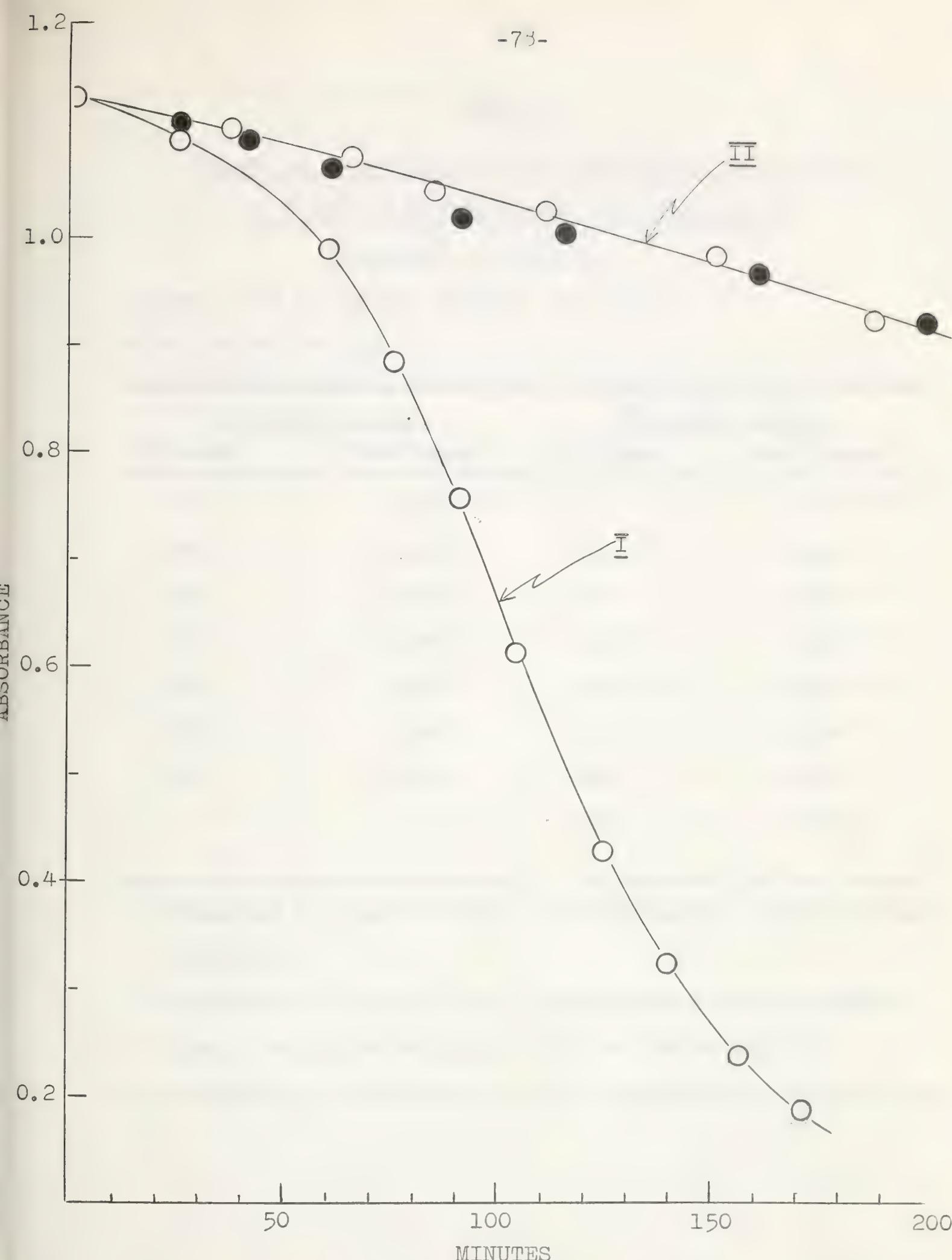


Fig. 7. Change in absorbance at 265 m μ during the reduction of nitrobenzene by I, 0.150 M Na₂S and II, 0.150 M NaHS (details overleaf). ● Contains 10% dissolved sulphur.

TABLE 6

Change in Absorbance at 265 m μ During The Reduction
of 0.0150 M Nitrobenzene by Sodium Hydro-
sulphide* (0.160 M)

Solvent, 40% by weight ethanol in water

Data plotted in Fig. 7.

<u>No added sulphur</u>		<u>10% added sulphur</u>	
Minutes	Absorbance **	Minutes	Absorbance **
0	1.130 ***	0	1.130 ***
37	1.102	25	1.107
64	1.076	35	1.090
84	1.045	60	1.065
110	1.025	85	1.018
150	0.983	115	1.004
187	0.925	160	0.970
		200	0.925

* Prepared by the addition of hydrochloric acid to sodium sulphide

** Blank cell contained the corresponding initial sodium (poly) sulphide solution, diluted and acidified.

*** Calculated from known initial nitrobenzene concentration.

point of view. Subsequent work has indicated that the protonated disulphide does reduce faster than hydrosulphide. Thus the slight increase in rate observed during hydrosulphide reduction was also partially due to the increasing concentration of hydrodisulphide.

It was decided to study the hydrosulphide reduction of nitrobenzene in more detail and the results of this work follow.

B. The reduction of nitrobenzene by hydrosulphide ion in aqueous solution.

1. Autocatalytic nature of hydrosulphide reduction of nitrobenzene

In this work it was found that the reduction of nitrobenzene by hydrosulphide ion is also an autocatalytic process, but not to as marked an extent as for the analogous reduction by sulphide ion. This was shown by following the decrease of nitrobenzene (Fig. 8) or the increase in sulphur as hydrodisulphide (Figs. 9 and 11) during the reduction. In all cases an acceleration of rate is noted for the first portion of the reaction. In following the reduction by measurement of the absorption of nitrobenzene at $267\text{m}\mu$, allowance for the absorption at $267\text{m}\mu$ due to phenylhydroxylamine was found to be necessary. Ogatas' technique (10) of acidification of the reduction mixture with hydrochloric acid and measurement of absorption of the residual nitrobenzene at $267\text{m}\mu$ was quite satisfactory for sulphide reductions of nitrobenzene since the hydrochloride of aniline, the only reduction product, gave negligible absorption at this wave length. However phenylhydroxylamine hydrochloride has an extinction coefficient at $267\text{m}\mu$ of 1.0×10^3 as compared with one of 7.4×10^3 for nitrobenzene. Since over the first 60 minutes of the hydrosulphide reduction of nitrobenzene, phenylhydroxylamine is essentially the

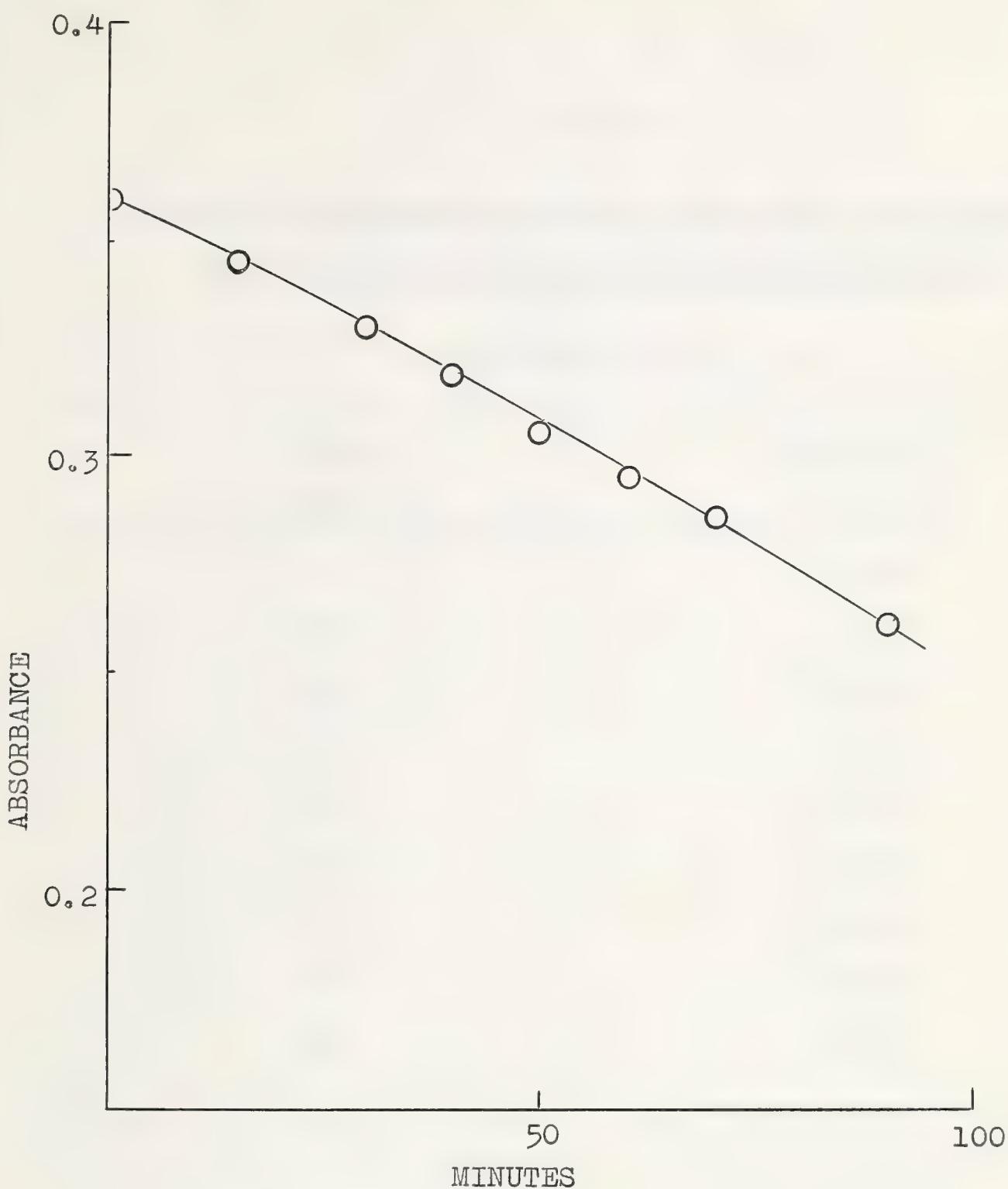


Fig. 8. Change in nitrobenzene concentration (absorbance at $267 \text{ m}\mu$) during its reduction with aqueous HS^- at 50°C . Initial nitrobenzene and HS^- concentrations, 0.0098 M and 0.150 M respectively.

TABLE 8

Decrease in Absorbance at 267 m μ During the Reduction
of 0.0098 M Nitrobenzene by Hydrosulphide Ion*

Data plotted in Fig. 8.

Time (Minutes)	Absorbance at 267 m μ
0	0.360
15	0.344
30	0.329
40	0.319
50	0.305
60	0.295
70	0.286
90	0.262
150	0.183

* Initial concentration, 0.150 M.

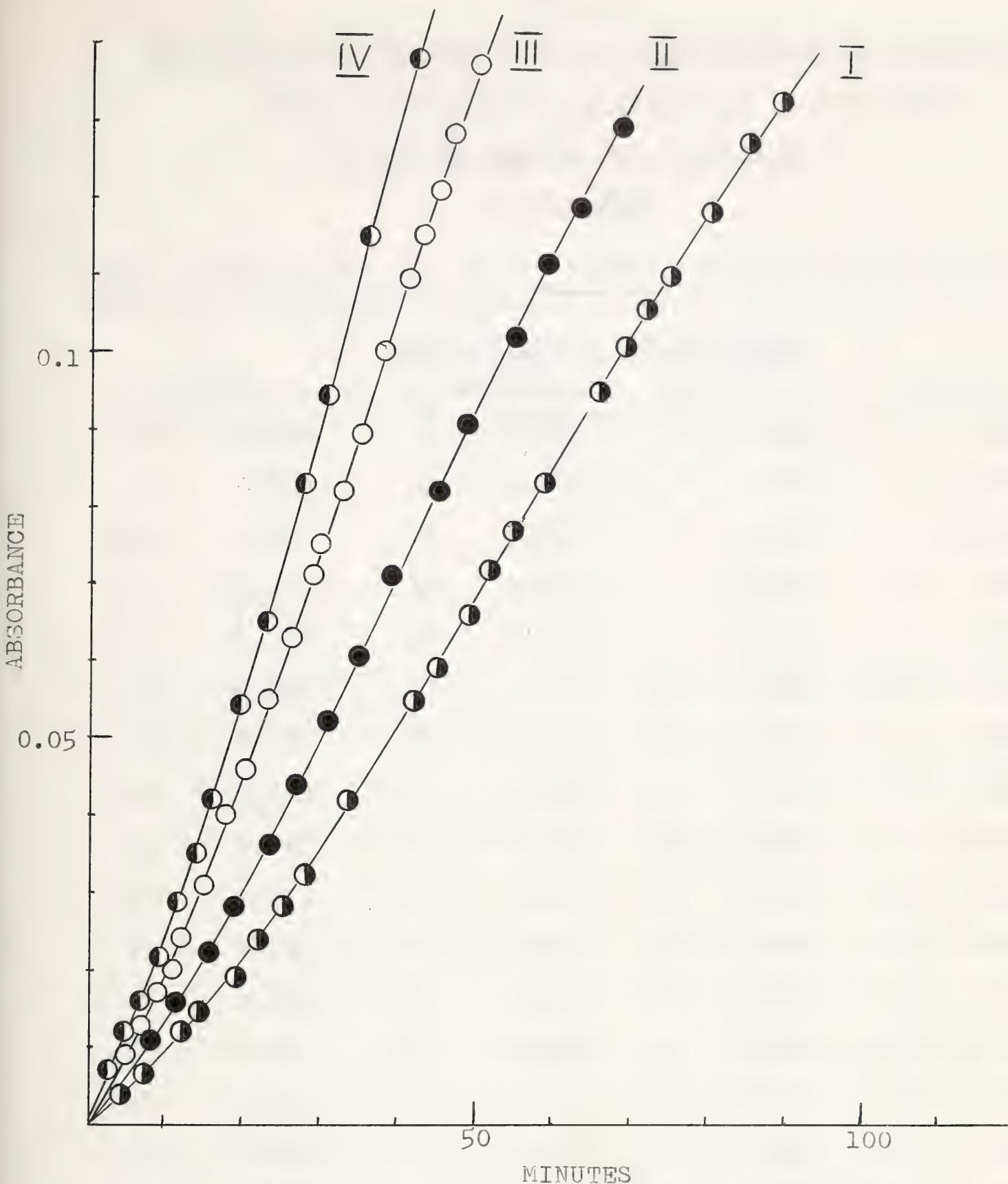


Fig. 9. Absorbance at 450 m μ of hydrodisulphide ion produced during the reduction of nitrobenzene by aqueous sodium hydrosulphide at 50°C. The initial concentration of nitrobenzene for all cases was 0.0094 M. Initial concentration of sodium hydrosulphide for runs I, II, III and IV was 0.150 M; 0.200 M, 0.250 M and 0.300 M respectively.

TABLE 9

The Effect of Varying Initial Hydrosulphide Ion Concentration on the Rate of Increase of Absorbance
at 450 m μ During the Reduction of
Nitrobenzene

Data plotted in Fig. 9. Nitrobenzene concentration 0.0094 M.

		<u>Hydrosulphide ion Molarity</u>					
0.150		0.200		0.250		0.300	
<u>t*</u>	<u>A**</u>	<u>t</u>	<u>A</u>	<u>t</u>	<u>A</u>	<u>t</u>	<u>A</u>
4	0.003	4	0.006	3	0.004	3	0.007
7	0.006	8	0.012	5	0.009	5	0.012
12	0.011	11	0.016	7	0.013	7	0.016
14	0.0135	16	0.023	9	0.017	9	0.022
19	0.018	19	0.028	11	0.020	12	0.029
22	0.023	23	0.036	12	0.025	14	0.035
28	0.031	27	0.044	15	0.031	16	0.042
34	0.041	31	0.052	18	0.040	20	0.055
37	0.045	35	0.061	20	0.046	23	0.065
42	0.054	39	0.071	23	0.055	28	0.083
45	0.057	45	0.082	26	0.063	31	0.095
49	0.066	49	0.091	29	0.071	36	0.115
52	0.071	55	0.102	30	0.075	42	0.138
55	0.076	59	0.111	33	0.083	47	0.153
59	0.083	63	0.119	35	0.089	52	0.175
66	0.095	68	0.131	38	0.100	58	0.196
69	0.100	73	0.138	41	0.110		
72	0.105	78	0.147	43	0.115		
75	0.109	85	0.160	45	0.121		
80	0.117			47	0.121		
85	0.127			50	0.137		
89	0.132						

* Time in minutes ** Absorbance at 450 m μ .

only product, and the amount of hydrodisulphide produced is still small, simultaneous loss of phenylhydroxylamine by reduction due to hydrodisulphide would thus be very small. Hence for this first portion of the reduction it is true that one molecule of phenylhydroxylamine is produced as one molecule of nitrobenzene disappears. Setting the drop in absorbance at $267\text{m}\mu$ due to disappearance of nitrobenzene equal to x and the corresponding increase in absorbance due to phenylhydroxylamine as $(1.0 \times 10^3 / 7.4 \times 10^3) x$, the true decrease in absorption of nitrobenzene becomes $x = 1.15 \times A_{\text{obs}}$ where A_{obs} is the observed absorption at $267\text{m}\mu$. This factor has been used to obtain the corrected initial slopes in the plot of nitrobenzene absorption vs time in both Figs. 8 and 12.

2. Dependence of the rate of nitrobenzene reduction on nitrobenzene and on hydrosulphide ion concentration.

Initial rates of appearance of hydrodisulphide, measured in terms of absorbance at $450\text{m}\mu$ were obtained from Fig. 9 for various initial concentrations of hydrosulphide ion. A plot of these initial rates against initial hydrosulphide ion concentration (Fig 10) clearly demonstrates a first order dependence of rate upon hydrosulphide ion concentration. It is interesting to note that this plot (Fig. 10) does not pass through the origin but intercepts the x (rate) axis at a negative value indicating that the rate expression is of the form

$$\frac{d(\text{HS}_2^-)}{dt} = k(\text{HS}_2^-)(\text{C}_6\text{H}_5\text{NO}_2) - C.$$

Here C is due to a constant contribution from the competitive reaction of hydroxyl ions with sulphur liberated initially. From the slope of this plot a value of the rate constant can be obtained.

RATE of INCREASE in ABSORBANCE at $450\text{m}\mu$

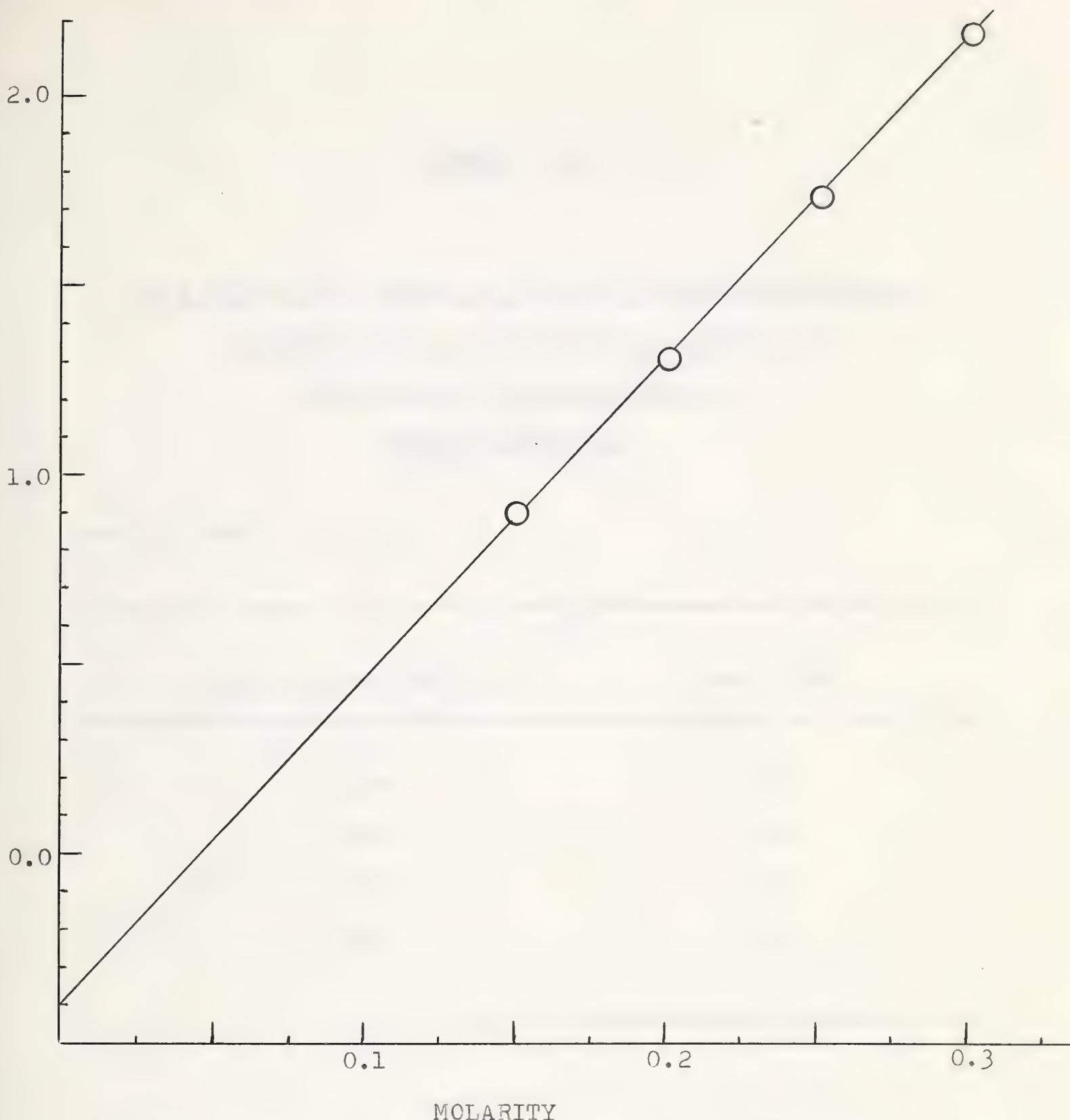


Fig.10. Plot of initial rates of reduction of nitrobenzene by hydrosulphide ion (obtained from Fig.9) vs initial hydrosulphide ion concentration (from Fig.9), demonstrating first order dependence of reaction rate on hydrosulphide ion concentration.

TABLE 10

The Effect of Change in Initial Hydrosulphide Ion
Concentration on the Initial Rates of
Reduction of Nitrobenzene by
Hydrosulphide Ion

Data plotted in Fig. 10.

Hydrosulphide Molarity	Rate* $\times 10^3$
0.150	0.90
0.200	1.31
0.250	1.74
0.300	2.18

* Rates, in terms of change in absorbance per minute,
obtained from Fig. 9.

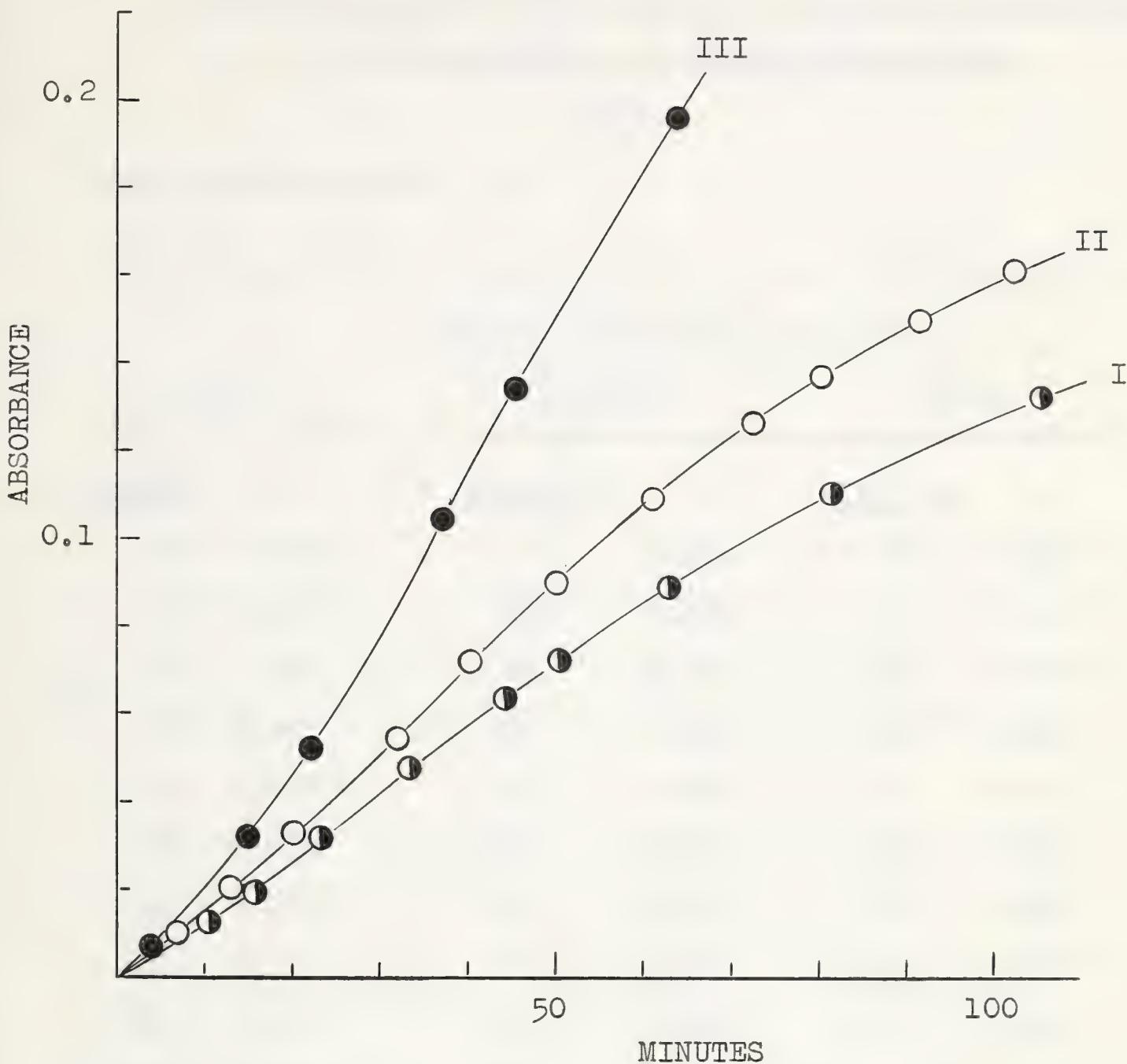


Fig. 11. The change in absorbance at $450 \text{ m}\mu$ due to HS_2^- formation during the reduction of nitrobenzene by 0.150 M aqueous HS^- solutions at 50.0°C . Initial nitrobenzene concentrations are 0.00680 M, 0.00790 M and 0.0131 M for plots I, II, and III respectively.

TABLE 11

The Change in Absorbance at 450 m μ During the Reduction
of Nitrobenzene by 0.150 M Hydrosulphide

Ion

Data plotted in Fig. 11.

Initial nitrobenzene molarity					
0.00680		0.00790		0.0131	
Minutes	A*	Minutes	A	Minutes	A
10	0.013	7	0.010	4	0.007
16	0.020	13	0.021	15	0.032
23	0.032	20	0.032	21	0.052
33	0.047	32	0.054	37	0.104
44	0.063	40	0.072	45	0.133
50	0.072	50	0.090	56	0.172
63	0.088	61	0.109	63	0.195
81	0.110	72	0.126	128	0.335
105	0.132	80	0.136	172	0.362
120	0.143	91	0.149		
137	0.153	102	0.161		
		192	0.203		

* Absorbance at 450 m μ

As the rates have been plotted in terms of absorbance change, the value of the slope must be divided by 35.0 (the extinction coefficient of hydrodisulphide at $450\text{m}\mu$). This gives a first order rate constant of $8.45 \times 10^{-3} / 35.0 = 2.41 \times 10^{-4} \text{ min}^{-1}$. Dividing this by the initial nitrobenzene concentration (0.00940 M in each case) a second order rate constant of $2.57 \times 10^{-2} \text{ liter mole}^{-1} \text{ min}^{-1}$ is obtained. This compares favorably with the value of $2.68 \times 10^{-2} \text{ liter mole}^{-1} \text{ min}^{-1}$ obtained from the data in Table 13 (see below). The close agreement supports the assumption made as to the course of the reduction and of the nature of the polysulphide (HS_2^-) produced in situ.

The dependence of the initial rate of disappearance of nitrobenzene upon initial nitrobenzene concentration is illustrated in Fig. 12. Using the initial rates of reaction (Table 13), it is seen that the reaction is first order in nitrobenzene concentration.

It is realized that the limited range of initial concentrations of nitrobenzene and of hydrosulphide ion used to demonstrate the order of reaction is unsatisfactory. The range is limited in the first place by the low solubility of nitrobenzene in water and secondly by the slowness of the reaction at lower hydrosulphide ion or nitrobenzene concentrations. In any case the order of reaction has already been adequately determined by Goldschmidt's work (52) and the present work serves to corroborate this by employing different analytical methods.

C. Comparison of ease of reduction of nitrobenzene by hydrosulphide and hydrodisulphide

In order to test the relative reducing abilities of hydrosulphide and hydrodisulphide at the pH (10.3) and temperature (50°)

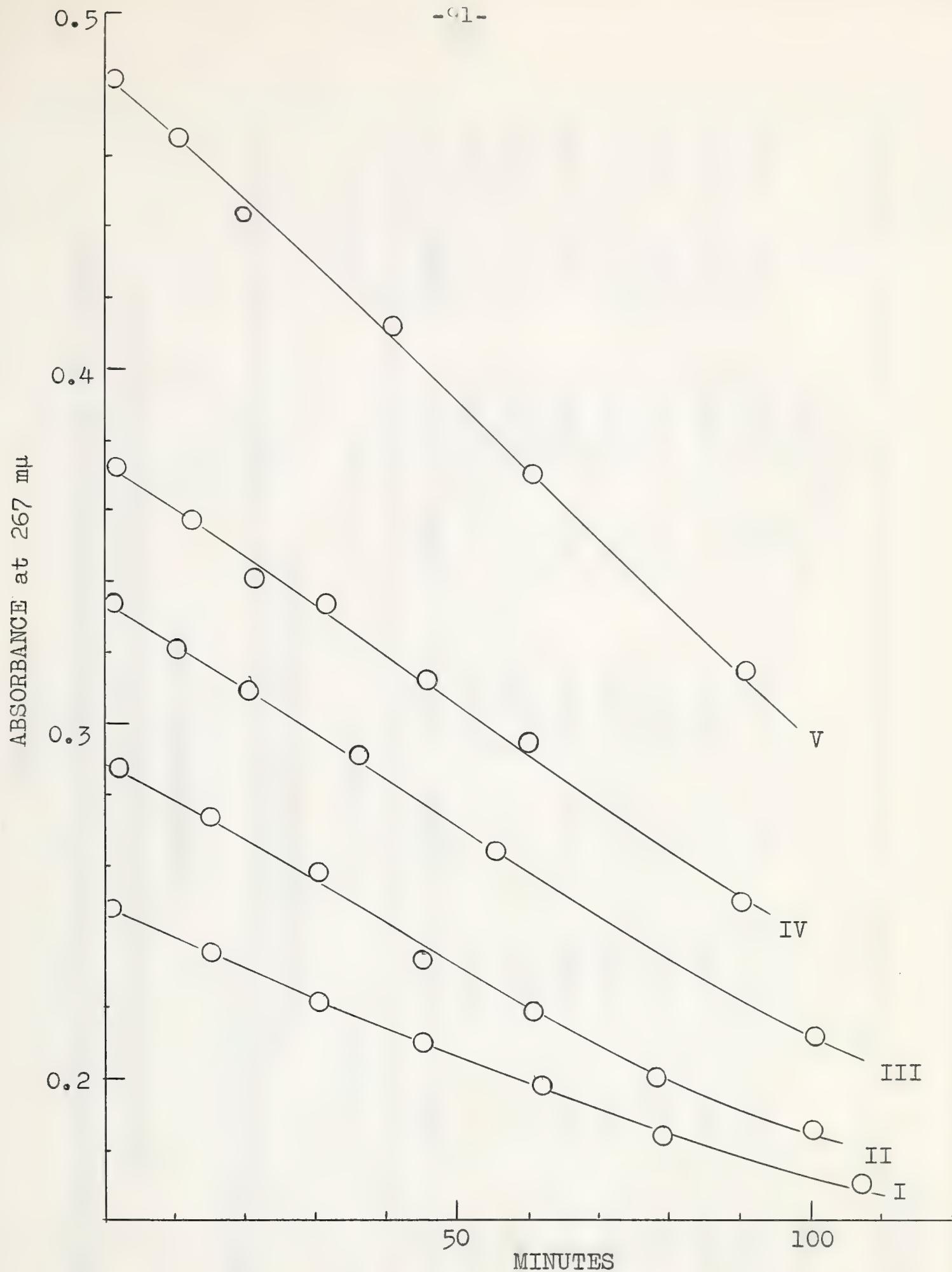


Fig. 12. Effect of change in initial nitrobenzene concentration on its rate of reduction by aqueous 0.150 M HS^- at 50.0°C . Initial nitrobenzene concentrations for runs I to V are 0.0068 M, 0.0079 M, 0.0102 M and 0.0132 M resp.

TABLE 12

The Effect of Change in Initial Nitrobenzene Concentration on the Rate of
Disappearance of Nitrobenzene During its Reduction by 0.150 M

Hydrosulphide Ion

Data plotted in Fig. 12.

Initial nitrobenzene concentration						
	0.0068 M	0.0079 M	0.0091 M	0.0102 M	0.0132 M	
Time * A **	Time * A **	Time * A **	Time * A **	Time * A **	Time * A **	Time * A **
1 0.248	2 0.287	1 0.333	1.5 0.371	1 0.481		
15 0.235	15 0.273	10 0.320	12 0.357	10 0.464		
30 0.222	30 0.258	20 0.309	21 0.340	20 0.441		
45 0.210	45 0.233	36 0.290	31 0.334	40 0.411		
62 0.198	60 0.219	55 0.264	45 0.312	60 0.370		
79 0.183	78 0.200	75 0.252	60 0.295	90 0.316		
107 0.171	100 0.185	100 0.212	90 0.250	125 0.251		
130 0.159			152 0.176			

* in minutes

** Observed absorbance at 267 m μ

TABLE 13

Dependence of Reduction of Nitrobenzene by Hydrosulphide Ion on Nitrobenzene Concentration

Initial nitrobenzene concentration (absorbance at 267 mu)	Rate of decrease in absorbance* at 267mu $\times 10^3$ (min $^{-1}$)	Rate of decrease in absorbance \div absorbance of nitrobenzene $\times 10^3$ (min $^{-1}$)
0.482	1.94	4.03
0.373	1.51	4.05
0.334	1.33	3.98
0.289	1.15	3.97
0.248	1.01	4.06

* Obtained from the initial slope of plots in Fig. 12, corrected by application of the relationship—"Corrected absorption of Nitrobenzene = 1.15 \times observed absorption". Initial slopes of the plots in Fig. 12 were multiplied by the factor 1.15 and these corrected slopes are recorded above in column 2.

of the solutions employed, one run was carried out wherein sufficient sulphur was predissolved in the 0.150 M solution of hydrosulphide to make it 0.0150 molar in hydrodisulphide. Fig. 13 shows that the deliberate addition of this sulphur as hydrodisulphide definitely accelerated the rate of reduction by a factor of 1.8 (after correction for interference of phenylhydroxylamine at 267 m μ). This information is evidence that hydrodisulphide ion does reduce nitrobenzene more readily than does hydrosulphide ion and that hydrodisulphide is the entity responsible for the auto-catalytic nature of the reaction. The conclusion made previously (see p.77) that hydrodisulphide and hydrosulphide in aqueous ethanol possessed comparable reducing abilities must now be modified for the reduction in completely aqueous media. It is likely that in aqueous ethanol the hydrodisulphide is also somewhat more effective than is hydrosulphide but the difficulty and consequent error involved in estimating the interference (due to sulphur) of the acidified hydrodisulphide at 265 m μ under those conditions could readily have masked the relatively small increase in rate due to hydrodisulphide. In the aqueous media used in the present work there was no comparable difficulty as the sulphur formed on acidification of the hydrodisulphide ion was completely precipitated (see Experimental section).

The initial reduction, quite evident in Fig. 8 and in Fig. 13 (plot I), is due chiefly to HS^- . A small contribution may arise from the unavoidable traces of hydrodisulphide present. However the fact that the rate of reduction was increased by a factor of only 1.8 when as much as 10% of the hydrosulphide was in the form of hydrodisulphide, shows that small traces of the latter as a

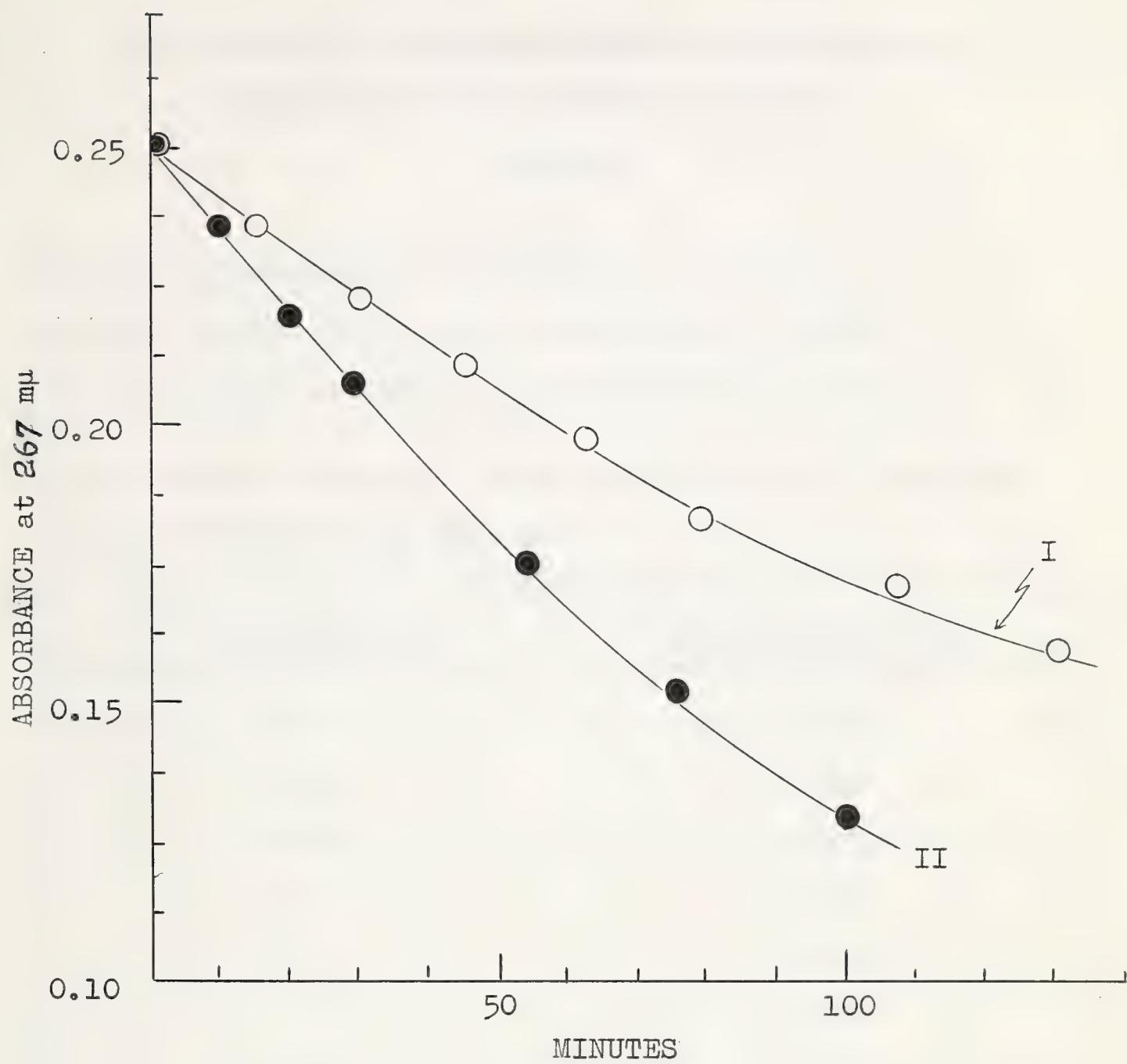


Fig. 13. The effect of addition of sulphur as hydrodisulphide to a solution of sodium hydrosulphide on the rate of reduction of nitrobenzene. Initial nitrobenzene concentration 0.0068 M. Plot I, reduction by 0.150 M HS^- . Plot II, reduction by 0.150 M HS^- containing 0.0150 M of dissolved sulphur as hydrodisulphide.

TABLE 14

The Effect of Dissolved Sulphur on the Rate of
Reduction of Nitrobenzene by Hydro-
sulphide

Initial nitrobenzene concentration, 0.0068 M.

Initial hydrosulphide ion concentration, 0.135 M.

Initial hydrodisulphide ion concentration, 0.015 M.

Data plotted in Fig. 13* (the data for plot I being the same as for plot I in Fig. 12)

Time (minutes)	Absorbance (267 m μ)
2	0.250
10	0.236
20	0.227
29	0.207
54	0.182
75	0.152
100	0.130

* The observed absorbances have been multiplied by a factor of 2 in Fig. 13.

contaminant could not have contributed much to the rate of reduction shown initially by the solution of sodium hydrosulphide.

Determination of rate constants for the hydrosulphide and hydrodisulphide reduction of nitrobenzene

An approximate value of the rate constant (k_1) for hydrosulphide reduction of nitrobenzene in aqueous media can be obtained from the data in Table 13. Using the expression $-dA_n/dt = k_1 [HS^-] A_n$ where A_n is the concentration of nitrobenzene in terms of absorbance, and noting that the average value of $(-dA_n/dt) / A_n = 4.02 \times 10^{-3} \text{ min}^{-1}$, k_1 becomes $2.68 \times 10^{-2} \text{ liter mole}^{-1} \text{ min}^{-1}$.

From this value of k_1 and with the information available in Fig. 13, it is now possible to obtain a value for the hydrodisulphide reduction rate constant, k_2 . Here it is assumed that the solution of elemental sulphur (S_8) in a large excess of sodium hydrosulphide produces only the species HS_2^- , although the solution may actually contain mixtures of higher polysulphides as contaminants. Accordingly, from Fig. 13, plot II, where $[HS^-] = 0.135 \text{ M}$, $HS_2^- = 0.015 \text{ M}$, the absorbance of nitrobenzene, $A_n = 0.500$ and the initial slope is $dA_n/dt = 3.5 \times 10^{-3} \text{ min}^{-1}$, appropriate substitution in the expression $-dA_n/dt = k_1 [HS^-] A_n + k_2 [HS_2^-] A_n$ gives $k_2 = 1.92 \times 10^{-1} \text{ liter mole}^{-1} \text{ min}^{-1}$.

Comparison of these rate constants shows that sodium hydrodisulphide reduces nitrobenzene about 7 times more rapidly than does sodium hydrosulphide.

D. The reduction of phenylhydroxylamine by hydrodisulphide ion

The reduction of phenylhydroxylamine by aqueous sodium hydrosulphide containing hydrodisulphide is due essentially to the

hydrodisulphide species. Hydrosulphide itself reduces the hydroxylamine very slowly (Table 7). Certainly in the first 90 minutes of reaction, reduction with a mixture of hydrosulphide and hydrodisulphide occurs practically only by hydrodisulphide with simultaneous decrease in the hydrodisulphide concentration. It has been possible to follow the reduction of phenylhydroxylamine during the first 90-100 minutes by measuring the decrease in absorption of hydrodisulphide at 450 μ . The results are shown in Fig. 14.

If it is assumed that the reaction between phenylhydroxylamine and hydrodisulphide is first order in each component, a value can be obtained for the rate constant, k_3 , for the disappearance of hydrodisulphide by use of the expression $- \frac{dA_{HS_2^-}}{dt} = k_3 [\text{hydroxylamine}][HS_2^-]$. From a measurement of the initial rate, $\frac{dA_{HS_2^-}}{dt} = 2.00 \times 10^{-3} \text{ min}^{-1}$, obtained from Fig. 14, where $A_{HS_2^-}$ is the absorbance of the hydrodisulphide, the concentration of the hydrodisulphide is 0.406 expressed as absorbance and the concentration of phenylhydroxylamine is 0.010 M, substitution in the above expression gives $k_3 = 5.1 \times 10^{-1} \text{ liter mole}^{-1} \text{ min}^{-1}$. This indicates that phenylhydroxylamine is reduced by hydrodisulphide about 2.7 times more rapidly than is nitrobenzene. This difference in rate explains the findings in Table 7, and the failure to find phenylhydroxylamine in nitrobenzene reduction by hydrodisulphide.

F. Source of hydropolysulphide in air-free hydrosulphide solutions

Considering the precautions taken to eliminate atmospheric oxygen, it is difficult to explain the slow appearance, in sodium hydrosulphide and sodium sulphide solutions, of the yellow colour characteristic of polysulphide solutions. In particular, as polysulphide solutions are actually oxidized by air to colourless

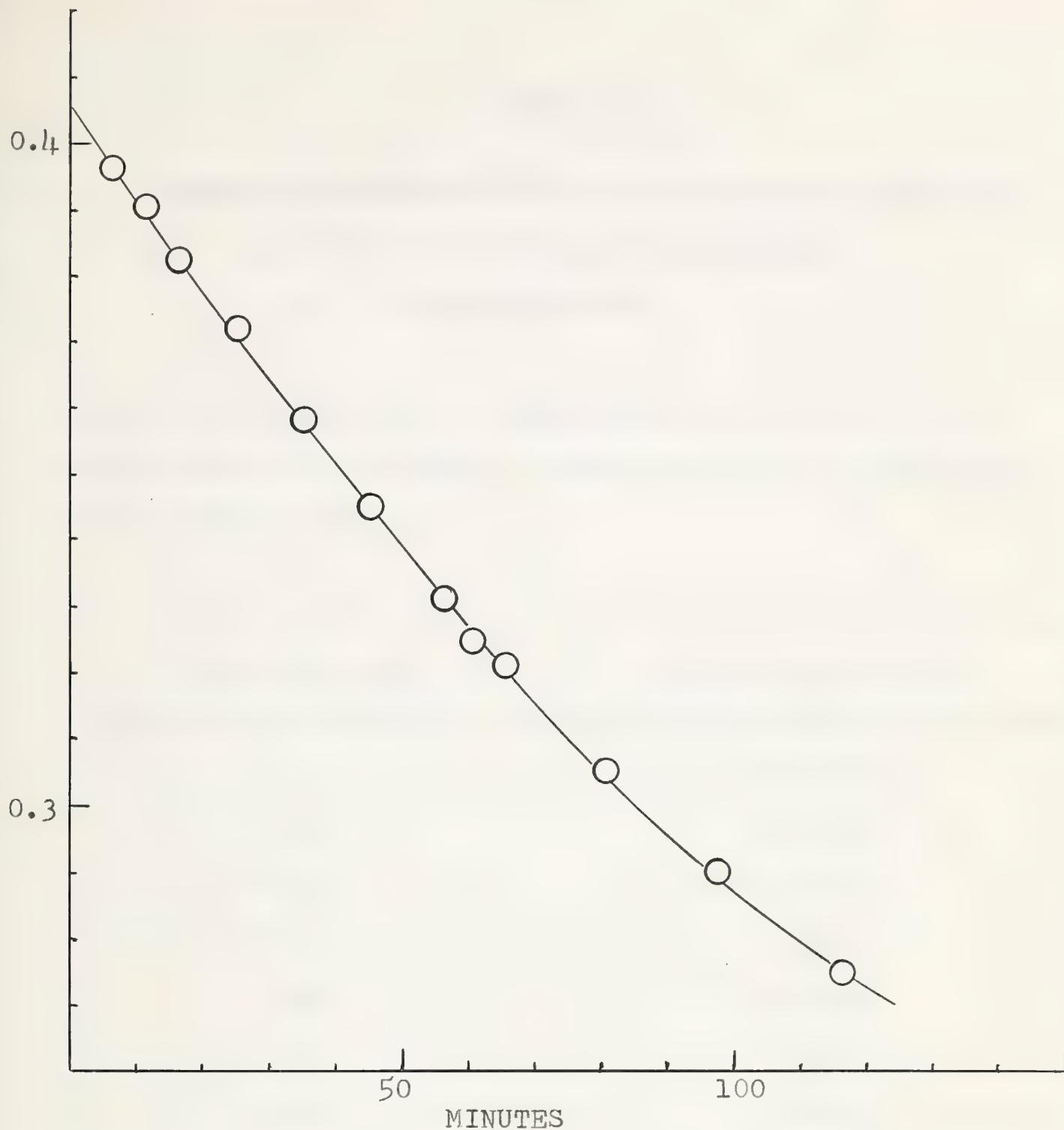


Fig.14. Disappearance of hydrodisulphide ion during the reduction of a 0.010 M solution of N-phenylhydroxylamine by 0.150 M aqueous sodium hydrosulphide containing sufficient elemental sulphur to convert about 8% of the hydrosulphide to hydrodisulphide.

TABLE 15

Change in Absorbance at 450 m μ During the Reduction
of N-Phenylhydroxylamine* by Hydro-
disulphide Ion

Initial concentration of hydrosulphide ion, 0.150 M,
containing 7.7% elemental sulphur as hydrodisulphide ion.
Data plotted in Fig. 14.

Time (minutes)	Absorbance (450 m μ)
0	0.405 **
6	0.396
11	0.390
16	0.382
25	0.372
35	0.358
45	0.345
56	0.331
60	0.325
65	0.321
80	0.305
97	0.290
116	0.275

* initial concentration 0.0100 M

** calculated

solutions, which as a result contain thiosulphate, it is necessary to explain the slow but definite appearance of polysulphide in these colourless solutions in the absence of air. Mellor (68) has explained this as a reaction between sulphide ion and thiosulphate ion. Thus a solution containing both sulphide ion and thiosulphate ions, when boiled in the absence of air, soon acquires the deep yellow colour characteristic of polysulphide solutions. Mellor has suggested that since one of the sulphur atoms in the thiosulphate ion is relatively loosely bound, it is removed by the sulphide ion to give polysulphide and sulphite ions according to the following equation:

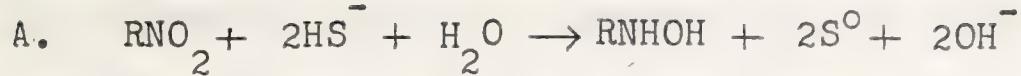


Thiosulphate is certainly present as an impurity in the sodium sulphide used in this work (see Experimental section). However, it was found during the course of this work that addition of excess sulphite ion to polysulphide solutions caused an immediate discharge of the solution's yellow colour. Apparently the reverse of the above reaction was taking place. The two observations can be reconciled, as the reaction indicated by equation r is considered to be an equilibrium (68). Thus at very low sulphite ion concentrations and in the absence of air the formation of small quantities of polysulphide is possible.

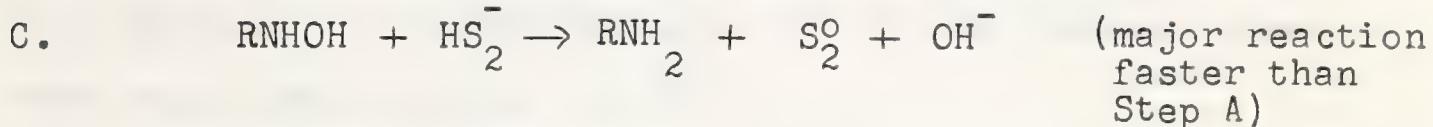
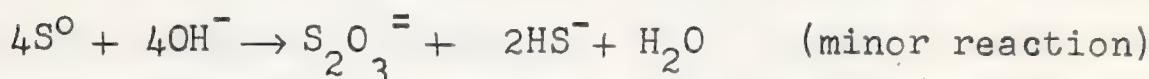
G. Summary of the course of reduction of nitrobenzene by aqueous sodium hydrosulphide

The results of the foregoing rate studies in conjunction with the stoichiometry presented in Part IV D. of this section, support the course of reduction of nitrobenzene by aqueous hydrosulphide ion which is represented by the following stepwise

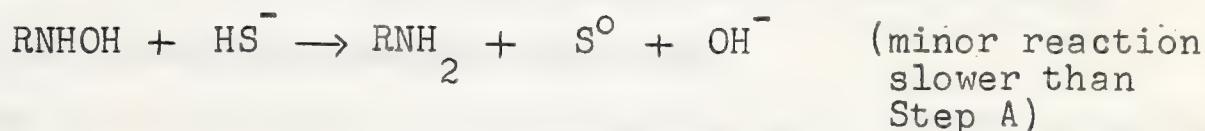
reactions.



and



and



D. Reaction of the sulphur produced in Step C according to reactions in Step B, except that the major reaction is now conversion of this sulphur to $\text{S}_2\text{O}_3^=$ rather than to HS_2^- .

From the data in Parts IV D and E of this section it is seen that approximately $2/3$ of the thiosulphate ion produced in the complete reduction of nitrobenzene comes from the sulphur obtained in Step C via the reduction of the phenylhydroxylamine, while the remaining $1/3$ arises from the sulphur produced by Step A. The preference of elemental sulphur, produced by Step C, to form $\text{S}_2\text{O}_3^=$ rather than HS_2^- while the major portion of the sulphur from Step A is converted to HS_2^- rather than $\text{S}_2\text{O}_3^=$ might be related to the greater degree of solvation of the phenylhydroxylamine. The prevalence of water molecules solvating the basic hydroxylamine portion would lead to rapid interaction between the liberated hydroxyl group with the elemental sulphur formed before much of the latter could escape into the bulk solution where the normal competitive reaction with OH^- and HS^- occurs.

The lower degree of solvation of the nitro group would enable the elemental sulphur to escape into the bulk solution more readily. However, in the latter case, the formation of this active sulphur in favorable juxtaposition with the hydroxyl ions also formed in the reduction of nitrobenzene by HS^- (Step A) would explain the considerable amount of $\text{S}_2^{\text{O}_3^=}$ formed in this reaction wherein the concentration of OH^- in the bulk solution is very much less than that of HS^- .

The possible role of $\text{S}_2^=$ in the reduction of nitrobenzene by aqueous sodium sulphide-ammonium chloride

By way of a footnote to the foregoing work on the reduction of nitrobenzene by hydrosulphide or hydrodisulphide ions it must be stated that the contribution of the $\text{S}_2^=$ species to the observed rates of reduction has been assumed to be negligible. This assumption may be a fallacious one. Using the results of Kuster and Heberlein quoted previously (p.10) it is seen that the hydrolysis constant value for disulphide ion (viz. 0.045) gives a $\text{S}_2^{\text{H}^-}/\text{S}_2^=$ ratio of 45:1 at the pH encountered in this work. Kuster and Heberlein indicate on the other hand that an aqueous one molar solution of disulphide ion is about 30% hydrolyzed (23). This corresponds to a hydrolysis constant of about 0.13 giving a $\text{S}_2^{\text{H}^-}/\text{S}_2^=$ ratio of 130:1 for the solutions used in this work. However the value of 0.045 is corroborated to some extent in the present work. On page 31 it was shown that a 4 M solution of sodium hydroxide was required to push the equilibrium $\text{S}_2^= + \text{H}_2\text{O} \rightleftharpoons \text{S}_2^{\text{H}^-} + \text{OH}^-$ largely to the left. If at this hydroxyl ion concentration the ratio $\text{S}_2^{\text{H}^-}/\text{S}_2^=$ is of the order of 1×10^2 , the K_h value would be 4×10^{-2} , i.e. close to the value 0.045.

A consideration of either of the two values obtained above for $S_2H^-/S_2^=$ indicates the presence of 1-2% of the $S_2^=$ species. In view of its very superior reducing ability to the S_2H^- ion (from Figs. 2 and 7 a factor of at least 10^2 in aqueous ethanol is suggested) it is probable that some, if not most, of the observed rate which has been attributed to HS_2^- was due to the $S_2^=$ species.

If the contribution of $S_2^=$ is indeed an important one, the principal modification to be applied to the rate studies is one of redefinition. Thus the rate constants obtained for the reduction of nitrobenzene and phenylhydroxylamine by HS_2^- must be redesignated as applying to the reduction of these compounds by both HS_2^- and $S_2^=$. The rate of reduction of nitrobenzene is then given by the expression

$$\text{Rate} = [PhNO_2] (k' [HS_2^-] + k'' [S_2^=])$$

which with the expression $K_h = [HS_2^-][OH^-] / [S_2^=]$ gives

$$\text{Rate} = [PhNO_2][HS_2^-] (k' + k'' [OH^-] / K_h)$$

Thus the rate constant k_2 obtained on page 97 is a composite of the individual contributions of $S_2^=$ and HS_2^- , i.e.

$$k_2 = k' + k'' [OH^-] / K_h$$

The value for the rate constant k_1 obtained on page 97 is of course unaffected by the foregoing considerations.

The important conclusions remain, as regards the autocatalytic effect of the disulphide (protonated or otherwise) generated during the reaction and as to the relative rates of reduction of nitrobenzene and phenylhydroxylamine by the mixture of $S_2^=$ and S_2H^- .

SECTION 2

RESULTS AND DISCUSSIONS

Part VI

The Relative Rates of Reduction of p-Alkylnitrobenzenes by Hydrosulphide Ion

A. Method of rate determination

Due to the difficulties involved in making accurate allowance for interfering polysulphide absorbance, a method for following the rate of disappearance of the p-alkylnitrobenzenes spectrophotometrically was abandoned. It was decided therefore to use the rate of appearance of polysulphide as a measure of the rate of reduction in each case. That this approach is a valid one can be seen from the following considerations.

The rate of appearance of polysulphide

The increase in absorbance at 450 μu is a measure of the rate of increase in hydrodisulphide concentration and is dependent on the following series of reactions. There is an initial very slow reduction of the nitro compound by the hydrosulphide ion to give sulphur and hydroxyl ions, according to the equation



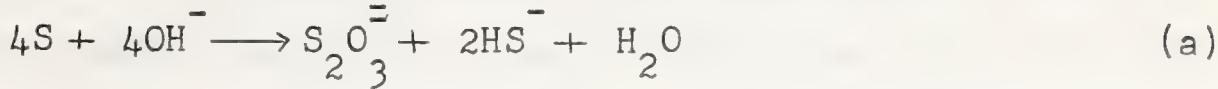
The further reduction of N-phenylhydroxylamine by hydrosulphide ion to aniline is a much slower reaction than that of nitrobenzene reduction shown in equation k. Hence N-phenylhydroxylamine accumulates at the expense of nitrobenzene as the reaction proceeds.

The sulphur, which is in a very reactive form (possibly atomic) quickly reacts with hydrosulphide ion to form hydrodi-

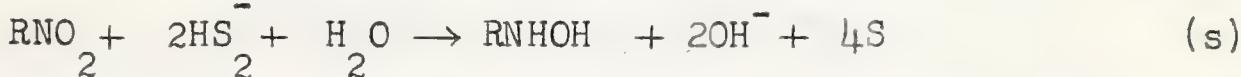
sulphide



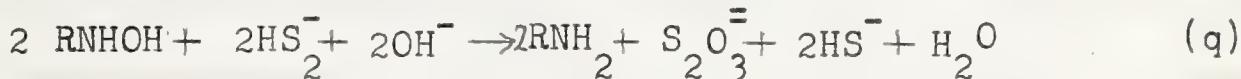
and also with hydroxyl ion to form thiosulphate



The hydrodisulphide thus formed also reduces the nitro compound slowly, but about seven times faster than does the hydrosulphide, to produce more active sulphur and hydroxyl ions



This sulphur will also be consumed via reactions p) and a). Subsequently, as the phenylhydroxylamine concentration increases hydrodisulphide ion is removed via the reaction



As this reaction is faster than the reduction of nitrobenzene by hydrodisulphide ion, the accumulated N-phenylhydroxylamine eventually disappears more quickly than does the nitrobenzene.

However if only the initial rate of formation of hydrodisulphide is considered, then it is apparent that at zero time when the concentration of hydrodisulphide ion is almost negligible, the contribution of reactions s and q to the overall rate can be neglected. If all the sulphur produced by reaction k were completely accounted for by reaction p, none going via reaction a, then the rate of appearance of hydrodisulphide would be given by

$$\frac{d(HS_2^-)}{dt} = k [HS^-] [RNO_2]$$

The proportion of sulphur reacting via equation p will be controlled by the relative concentration of hydrosulphide ions to

hydroxyl ions. As hydrosulphide ion is initially present in fairly large excess its concentration can be considered as remaining approximately constant for some time after the reaction has started. Likewise hydroxyl ion concentration remains essentially constant for most of the reaction due to the buffered nature of the reduction solution. If a fraction α of the sulphur reacts via equation p, then the rate of formation of hydrodisulphide is given by

$$\frac{d(HS_2^-)}{dt} = \alpha k [HS^-][RNO_2^-]$$

Accordingly, in comparing the relative rates of reduction of two different nitro compounds, if the initial concentration of hydrosulphide ion is the same in each case, the value of α will also be the same in each case. In addition, by making the initial concentrations of the different nitro compounds the same, the ratio of their respective rate constants can be obtained directly from the ratio of their corresponding initial reaction rates. In this case the rate of increase of absorbance at 450 μ m at zero time is a measure of the initial reaction rate.

B. Results of the relative rate study

The above reasoning was then applied to a comparison of the relative reducing rates of some para-alkyl substituted nitrobenzenes. The compounds considered in addition to unsubstituted nitrobenzene were p-methyl-, p-ethyl-, p-isopropyl-, p-t-butyl- and p-cyclohexylnitrobenzene. Conditions were arranged so that initial concentrations of hydrosulphide and nitro compound in each case were identical.

The original intention had been to carry out this comparison using sodium sulphide as the reducing agent. However, because

of the simultaneous oxidation of the methyl group of para-nitrotoluene by the alkaline polysulphide as discussed in the introduction (see also the Experimental section), this approach was abandoned. It was established that no comparable oxidation took place when hydrosulphide ion was used as the reducing agent. Acidification of the final reduction mixture produced no deep red colour, as was observed when sodium sulphide was the reducing agent (see Experimental).

In the cases of the para-methyl and para-t-butyl nitrobenzenes it was shown that the final product of reduction was the corresponding amine in each case (see Experimental).

The greater reducing power of hydrodisulphide compared with hydrosulphide made it imperative that the initial concentrations of this contaminating hydrodisulphide be identical in all reduction rate determinations. This required each reduction to be carried out at least twice and usually three or four times, in order to obtain a comparable series. The effect of a small change in initial concentration of hydrodisulphide is demonstrated in Fig. 15 for the reduction of p-nitrotoluene (0.0250 M) by 0.150 M hydrosulphide ion. Plot I, Fig. 15 is that for the reduction of a solution with initial absorbance of hydrodisulphide at $450\text{m}\mu$ of 0.023, whereas plot II, Fig. 15 is a composite of two such reductions where the initial absorbances at $450\text{m}\mu$ are only 0.006 and 0.008. The latter plot also demonstrates the degree of reproducibility of the measurements when all initial concentrations are practically the same.

A comparable series, obtained as outlined above, is shown in Fig. 16. Solutions for all five runs had an initial absorbance at $450\text{m}\mu$, due to contaminating polysulphide, of 0.025 ± 0.002 .

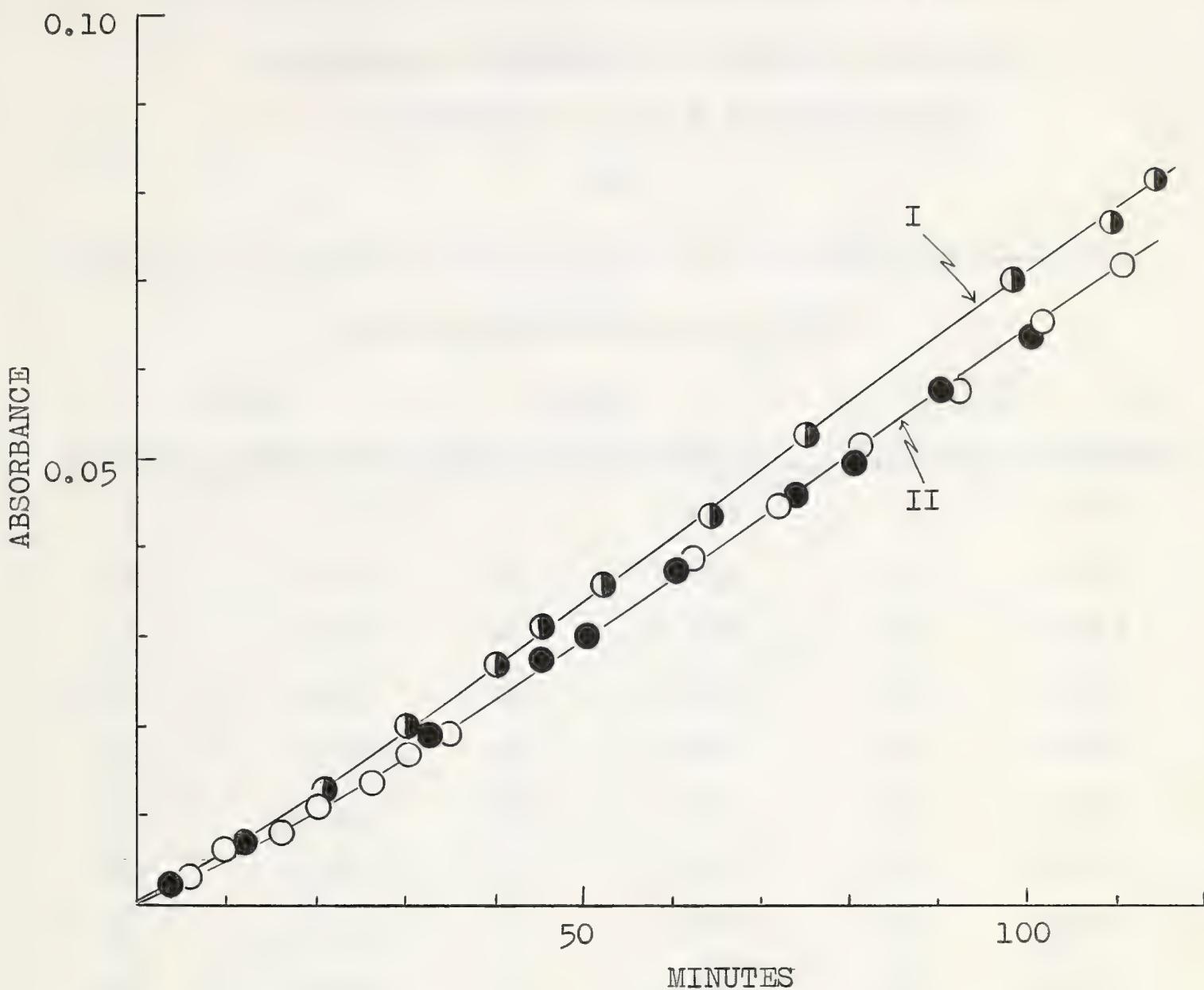


Fig. 15. The reduction of 0.0250 M p-nitrotoluene with 0.150 M HS^- in aqueous media. The effect of initial small amounts of contaminating HS_x^- on the relative rate of reduction. Plot I-for 0.150 M HS^- containing HS_x^- whose concentration is expressed by an absorbance of 0.023 at 450 $\text{m}\mu$. Plot II--two separate reductions, initial absorbances of HS_x^- at 450 $\text{m}\mu$ being 0.008, \bigcirc and 0.006, \bullet .

TABLE 16

The Effect of Initial Low Concentrations of HS_x^- on
the Rate of Reduction of 0.0250 M p-Nitro-
toluene by 0.150 M Hydrosulphide

Ion

<u>Initial Absorbance at 450 μ</u>					
	<u>0.006</u>		<u>0.008</u>		<u>0.023</u>
Minutes	Absorbance	Minutes	Absorbance	Minutes	Absorbance
3	0.002	4	0.003	6	0.003
12	0.007	10	0.006	12	0.007
33	0.019	16	0.008	21	0.013
50	0.030	20	0.011	30	0.020
60	0.038	26	0.014	40	0.027
73	0.046	30	0.017	45	0.031
80	0.050	35	0.019	52	0.036
90	0.058	62	0.039	64	0.044
100	0.065	72	0.045	75	0.053
138	0.090	81	0.052	98	0.071
		92	0.058	109	0.077
		101	0.066	114	0.082
		110	0.072	120	0.086
		121	0.080		
		133	0.087		
		140	0.092		

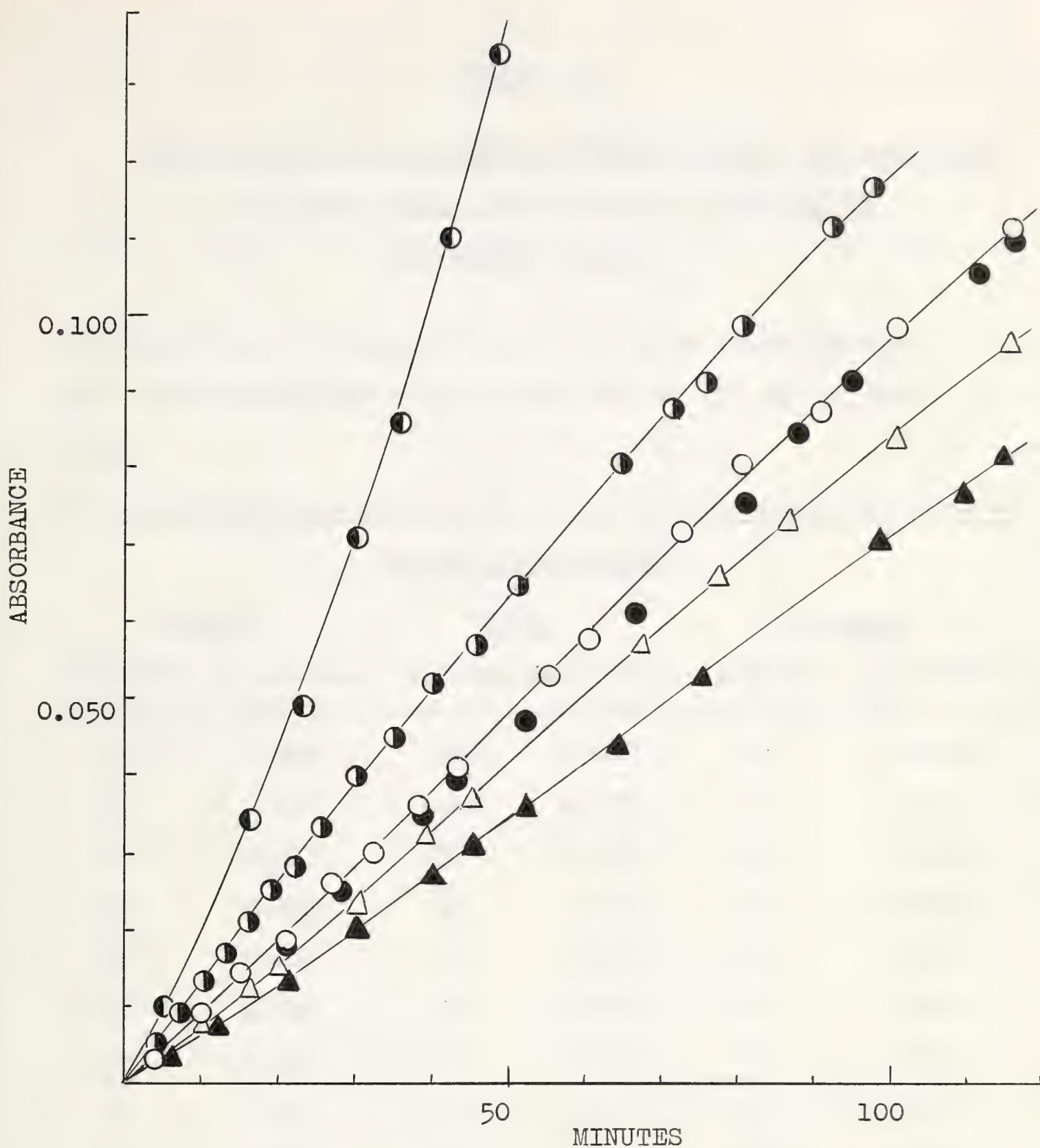


Fig.16. The change in absorbance at 450 m μ during the reduction of the p-alkylnitrobenzenes (0.0250 M) by 0.150 M hydrosulphide ion in 76.5% by weight ethanol in water at 50.0°C. The alkyl groups are H-, \bullet ; CH_3^- , \blacktriangle ; C_2H_5^- , \triangle ; cyclo- $\text{C}_6\text{H}_{11}^-$, \bullet ; $\text{i-C}_3\text{H}_7^-$, \circ and $\text{t-C}_4\text{H}_9^-$, \bullet .

TABLE 17

The Change in Absorbance at 450 m μ During the Reduction
of the p-Alkylnitrobenzenes(0.0250 M) by
Hydrosulphide Ion

Solvent 76.5% by weight ethanol in water contaminating HS_2^- had an absorbance of 0.025 ± 0.002 at 450 m μ in each case.

<u>p-Alkylnitrobenzene</u>					
	<u>Methyl</u>		<u>Ethyl</u>		<u>Cyclohexyl</u>
Minutes	Absorbance	Minutes	Absorbance	Minutes	Absorbance
6	0.003	10	0.007	10	0.009
12	0.007	16	0.012	18	0.016
21	0.013	20	0.015	21	0.019
30	0.020	30	0.023	28	0.027
40	0.027	39	0.032	38	0.037
45	0.031	45	0.037	43	0.041
52	0.036	67	0.057	52	0.049
64	0.044	77	0.066	66	0.063
75	0.053	86	0.073	74	0.067
98	0.071	100	0.084	80	0.078
109	0.077	115	0.097	87	0.087
114	0.082	129	0.109	94	0.093
120	0.086			111	0.108
130	0.093			115	0.112
				125	0.123

* The "blank" absorbance subtracted from all the observed absorbances
(continued)

TABLE 17, continued

<u>p-Alkylnitrobenzene</u>					
<u>i-Propyl</u>		<u>t-Butyl</u>		<u>Hydrogen</u>	
Minutes	Absorbance	Minutes	Absorbance	Minutes	Absorbance
4	0.003	4	0.005	5	0.010
10	0.009	7	0.009	16	0.034
15	0.014	10	0.013	23	0.049
21	0.018	13	0.017	30	0.071
27	0.026	16	0.021	35	0.086
32	0.030	19	0.025	41	0.110
38	0.036	22	0.028	48	0.134
43	0.041	25	0.033	58	0.166
55	0.053	30	0.040	65	0.186
60	0.058	35	0.045		
72	0.072	40	0.052		
80	0.081	45	0.057		
90	0.088	51	0.065		
100	0.099	64	0.081		
115	0.112	71	0.088		
130	0.124	75	0.092		
		80	0.099		
		92	0.113		
		97	0.118		

The results of the reductions of the p-alkylnitrobenzenes, shown in Fig. 16, certainly indicate a qualitative order of electron release in the sequence methyl > ethyl > i-propyl \simeq cyclohexyl > t-butyl > hydrogen. Quantitatively, the initial slopes in each case give a measure of the relative reduction rate constants of the nitro compounds, on the basis of the reasoning outlined above. The reductions were carried out, as before, at $50.00 \pm 0.03^{\circ}\text{C}$ and the initial concentrations of hydrosulphide ion and the nitrobenzene were 0.150 M and 0.0250 M respectively in each case. The solvent was 76.5% by weight ethanol in water. The following relative rate constants for the reduction of the p-alkylnitrobenzenes were obtained from the initial slopes of the plots in Fig. 16.

<u>Substituent</u>	Hydrogen	Methyl	Ethyl	i-Propyl	t-Butyl
<u>Relative rate Constants</u>	1.0	0.33	0.39	0.46	0.65

As indicated, these results were obtained for the reductions in 76.5% by weight ethanol in water. It has been suggested, as will be considered in more detail in the subsequent discussion, that the Baker-Nathan effect is actually a solvent effect rather than due to the electron release implied in the original concept of the term hyperconjugation (see references in the discussion below, Part VI C). It was hoped that in this work observations could be made on the effect of change of solvent on the relative rates of reduction of the para-alkyl nitrobenzenes. Unfortunately the compatibility and solubilities of both nitro compounds and the inorganic reagents required for reduction greatly limited the choice of solvents. The work was thus of necessity confined to

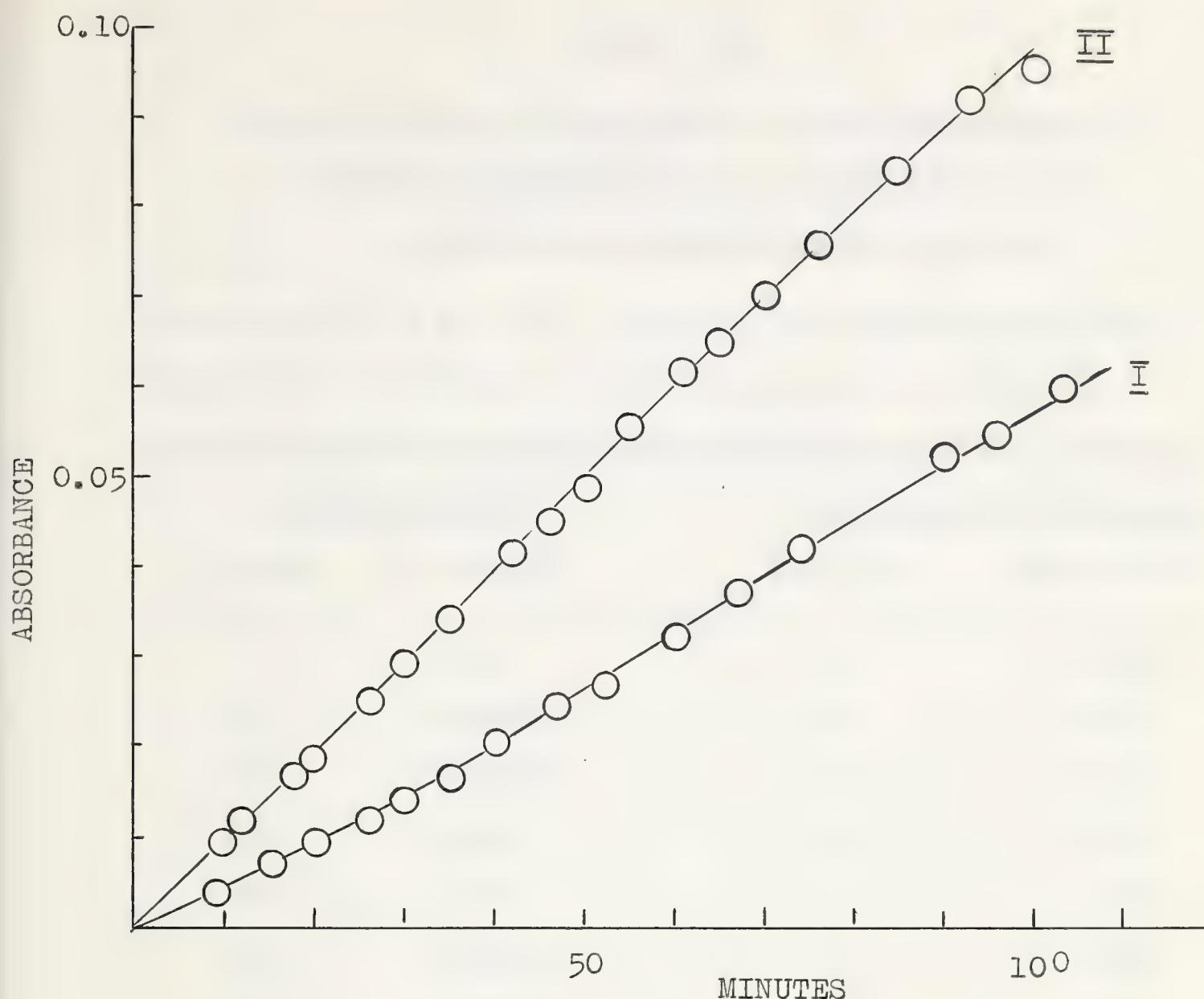


Fig. 17. Change in absorbance at 450 m μ during the reduction of I, 0.0250 M p-nitrotoluene and II, 0.0250 M p-t-butylnitrobenzene by 0.150 M hydrosulphide ion in 51.5% by weight ethanol in water.

TABLE 18

Relative Rates of Reduction of p-Nitrotoluene and
p-t-Butylnitrobenzene by Hydrosulphide Ion
in 50.5% by Weight Ethanol in Water

Data plotted in Fig. 17. Initial concentration of hydrosulphide, 0.150 M and of the nitrobenzene, 0.0250 M.

<u>p-nitrotoluene</u>		<u>p-t-butyl nitrobenzene</u>	
Minutes	Absorbance*	Minutes	Absorbance*
7	0.002	10	0.0095
12	0.0055	12	0.012
20	0.0095	18	0.017
26	0.012	20	0.019
30	0.014	26	0.025
35	0.0165	30	0.029
40	0.0205	35	0.034
47	0.0245	42	0.042
52	0.027	46	0.045
60	0.032	50	0.049
67	0.037	55	0.055
74	0.042	61	0.062
90	0.052	65	0.065
96	0.055	70	0.070
103	0.060	76	0.076
		85	0.084
		93	0.092
		100	0.096

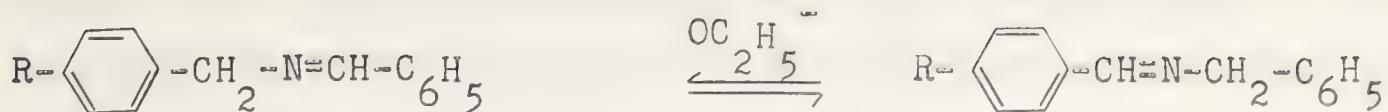
* 450 m μ

the use of aqueous alcoholic solutions containing not more than 50% nor less than 20% water. Accordingly, only the two extremes of alcohol water mixtures compatible with the solutes were used to demonstrate the effect of change in solvent composition on the relative rates of reduction. It was found, (Fig. 17) that the ratio (1:2.0) of the initial reduction rates of p-nitrotoluene and p-t-butylnitrobenzene in a solution 50.5% by weight ethanol in water was identical (within experimental error) with the value found in 79% ethanol in water (Fig. 16)

C. Discussion of the results in terms of the Baker-Nathan effect

The original concept of hyperconjugation, as proposed by Baker and Nathan (69) suggested the existence of a second means of electron release by alkyl groups in addition to the normal inductive mechanism. They suggested that when a methyl group is attached to a conjugated system, the electron duplet forming the carbon-hydrogen bond is appreciably less localised than that in a similarly placed carbon-carbon bond. Thus this auxilliary mode of electron release, sometimes referred to as "no-bond resonance" is tautomeric in nature. On the basis of electron release solely by the inductive mechanism, the order of increasing electron release is given by hydrogen < methyl < ethyl < i-propyl < t-butyl. However, if hyperconjugation is the predominant mode of electron release, the alkyl group containing the most alpha carbon-hydrogen bonds will provide the largest electron release; the order becoming hydrogen < t-butyl < i-propyl < ethyl < methyl.

In the first place Baker and Nathan demonstrated that this electron release was electromeric in nature. Thus in the face of high electron demand in the transition state or activated complex it is brought into play, not having been present in the ground state of the molecule. Later Baker, Nathan and Shoppee (70) demonstrated that this electron release could also be mesomeric in nature. In other words it could be present in the ground state of the molecule. This had to be tested in a reaction normally facilitated by electron recession from the reaction center, i.e. a reaction retarded by the presence of electron releasing groups. They illustrated this mesomeric nature of hyperconjugation with the sodium ethoxide catalyzed prototropy of benzylidene para-alkylated benzylamines; i.e. for the reaction.



(where R-was H-, CH_3- , $\text{i-C}_3\text{H}_7-$ and $\text{t-C}_4\text{H}_9-$)

The ionisation of carboxylic acids is also a reaction facilitated by electron recession from the reaction site, which in this case is the hydroxylic oxygen. The ionisation constants of the para-alkylated benzoic and phenylacetic acids have been examined (71) and appear to exhibit a general reversal of the inductive order of electron release, although with some jumbling of the order in the case of the benzoic acids.

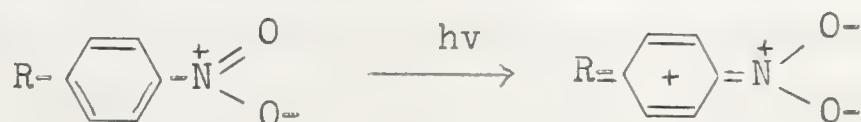
The hypothesis of hyperconjugation has become the subject of much study and also much controversy in the two decades since it was first proposed (69). When physical measurements have been used to assess the relative electron releasing ability of the alkyl groups, the normal inductive order of electron release has been observed. This has been the case, for example, with the dipole moments (72) and the ionization potentials (73) of the alkylbenzenes. However, in many rate and equilibria studies, a partial or total inversion of the inductive order has been found (74 & 75). This has been interpreted by several authors in terms of a solvent effect (76-79) and also as a steric effect (80), rather than as a mechanism of electronic origin. Schubert suggested that the apparent contradiction between chemical and physical data can be resolved by taking the role of solvent stabilisation into account. Thus in terms of ring solvation the methyl group would provide less steric hindrance than the t-butyl group to solvation near the site of attachment of the alkyl group (76).

Shiner (77) likewise, considered the role of the solvent as enhancing carbon-hydrogen hyperconjugation over carbon-carbon hyperconjugation by hydrogen bonding of the solvent with the alpha hydrogens of the alkyl group. Clement and Naghizadeh (79) have been able to relate solvation energy to the Baker-Nathan effect exhibited in the methanolysis of p-methyl and p-t-butylbenzyl chlorides. Thus the t-butyl compound, which underwent methanolysis more slowly than the corresponding methyl compound, was also shown to be less strongly solvated than the methyl compound.

Burawoy and Spinner (80) neglected solvent considerations completely and considered the alkyl group as releasing electrons by an inductive mechanism only. Hyperconjugation was then ascribed to steric hindrance to bond contraction of the carbon-carbon bond between the alkyl group and the benzene ring. The hindrance should be larger for t-butyl than for methyl.

In turning to the problem of the p-alkyl nitrobenzenes, it is well established that the reduction of aromatic nitro compounds is facilitated by electron recession from the reaction centre; i.e. by electron withdrawing groups. This has been shown to be true for stannous chloride (81), titanous chloride (82 & 83) and sodium disulphide reductions (10).

Schubert et al. have studied the ultra-violet spectra of the p-alkylated nitrobenzenes in the gaseous state and in a variety of solvents (84). The excitation process, represented by



is considered to involve a π to π^* transition to a dipolar excited

state and is responsible for the "principal band" in the ultra-violet spectrum. This excitation process produces a large electron demand on the para-alkyl group. Using the wavelength of the "principal band" as a measure of the electron contribution of a substituent, an electron donating group would be expected to produce a bathochromic and an electron withdrawing group a hypsochromic shift, relative to unsubstituted nitrobenzene. Thus the alkyl group providing the largest electron release will produce the largest bathochromic shift. Using this criterion, it was found that in the gaseous phase the normal inductive order was obtained. However, in basic solvents such as water and alcohol a jumbling of the order appeared, tending towards the hyperconjugative order. In acidic solvents like 70% perchloric acid, or in non-polar solvents such as heptane, the tendency was towards the inductive order. However Rao et al. claim that these results may be partly explained as being "due to the uncertainty in the mechanism of the substituent effects on the transition." (85). Elsewhere, (86) Rao concludes, in view of conflicting interpretations in the literature, "the evidence for hyperconjugation from the absorption spectra of alkyl substituted benzene derivatives is not definitive."

In any case the role of the solvent in apparently modifying electron release is not completely explained by Schubert's hypothesis. Stock and Himoe (87) have studied the effect of solvent on the rates of chlorination of toluene and t-butylbenzene. The reaction was first of all examined in six acetic acid solvents varying in water content from 0.0 to 27.6 M. This variation produced no significant change in the relative chlorination rates of

the two compounds, which were in the hyperconjugative order. The reaction was further examined (88) in various structurally different solvents and again this produced no change in the relative rate, beyond the variation expected for the observed reagent selectivity. Stock concluded from this work that the Baker-Nathan effect is to be identified with a polar influence rather than a solvent effect. On the other hand, nitration of toluene and *t*-butylbenzene in a variety of solvents showed a consistent inductive order of relative substitution rates (89).

The present work on the reduction of the para-alkylnitrobenzenes does not offer any new insight as to the origin of Baker-Nathan effect, but merely provides another example of its existence in a reaction facilitated by electron recession from the point of attack. The limitations to solvent variation in the reaction under study has precluded any attempt to relate the observed Baker-Nathan order to any possible solvent effect. It was qualitatively established however that the *t*-butyl compound was less soluble in water than the methyl compound and presumably it follows that in the aqueous ethanolic reaction solvent the *t*-butyl compound would also be less solvated than the methyl compound. On the basis of Schubert's hypothesis, the *t*-butylnitrobenzene would have a less negative entropy of activation than *p*-nitrotoluene thus accounting for the observed rate order.

SECTION 3

EXPERIMENTAL

Part I

Chemicals, Solvents and Solutions.

A. Chemicals

Sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), obtained from the Nichols Chemical Company, was of reagent grade. It was colourless and apparently free from the yellowish polysulphide impurities found in sodium sulphide obtained from some other sources. Before being weighed, each crystal of the sulphide was carefully wiped free from any adhering moisture.

Sulphur was Merck sublimed material, used without further purification.

Nitro Compounds

Nitrobenzene was Fisher certified reagent grade material. This was distilled before use at $85^\circ - 86^\circ\text{C}$ at 10 mm. (90).

p-Nitrotoluene - was Fisher reagent material, which was recrystallized from ethanol and melted sharply at 51.5°C . Lit.m.p. $51.8-52.0^\circ$ (91).

p-Ethynitrobenzene, p-i-propynitrobenzene, p-cyclohexylnitrobenzene and p-t-butylnitrobenzene were all prepared by nitration of the corresponding alkylbenzenes. The mixtures of isomers were separated by fractional distillation until a constant refractive index was obtained. The p-t-butylnitrobenzene was purified further by two successive crystallizations from methanol. The p-cyclohexylnitrobenzene was also recrystallized twice from ethanol.

Observed Physical Properties of Compounds Prepared

p-alkylnitrobenzene and Preparation Reference	B.P. $^{\circ}$ C. obtained	M.P. $^{\circ}$ C. obtained	Refractive index
p-ethyl (92)	120/10mm. Lit., 126/13mm. (92)	-	1.5457 @ 20 $^{\circ}$ C. Lit. 1.5459 (92)
p-isopropyl (93)	132/12mm. Lit., 134/13mm. (94)	-	1.5355 @ 25 $^{\circ}$ C. Lit., 1.5352 @ 25.5 $^{\circ}$ C. (84)
p-cyclohexyl (95)	-	58 Lit., 58.5 (95)	-
p-tert.-butyl (96)	-	28 Lit., 28.4 (84)	-

N-Phenylhydroxylamine was prepared as described in "Organic Syntheses" (97) by the reduction of nitrobenzene with zinc dust. The crude product was recrystallized twice from skellysolve to give fine, colourless needles which melted sharply at 82 $^{\circ}$ C. By storing it at -20 $^{\circ}$ C., the compound remained unchanged and colourless indefinitely.

Aqueous ethanol (40%) was prepared by addition of the requisite amount of distilled water to 95% ethanol. This solution was deaerated before use by gentle reflux and subsequent cooling under an atmosphere of oxygen-free nitrogen.

B. Solutions

The Beer's law plots for the nitrobenzene solutions are given in Fig. 18 and are based on the values determined at 25 $^{\circ}$ C which are recorded in Table 19.

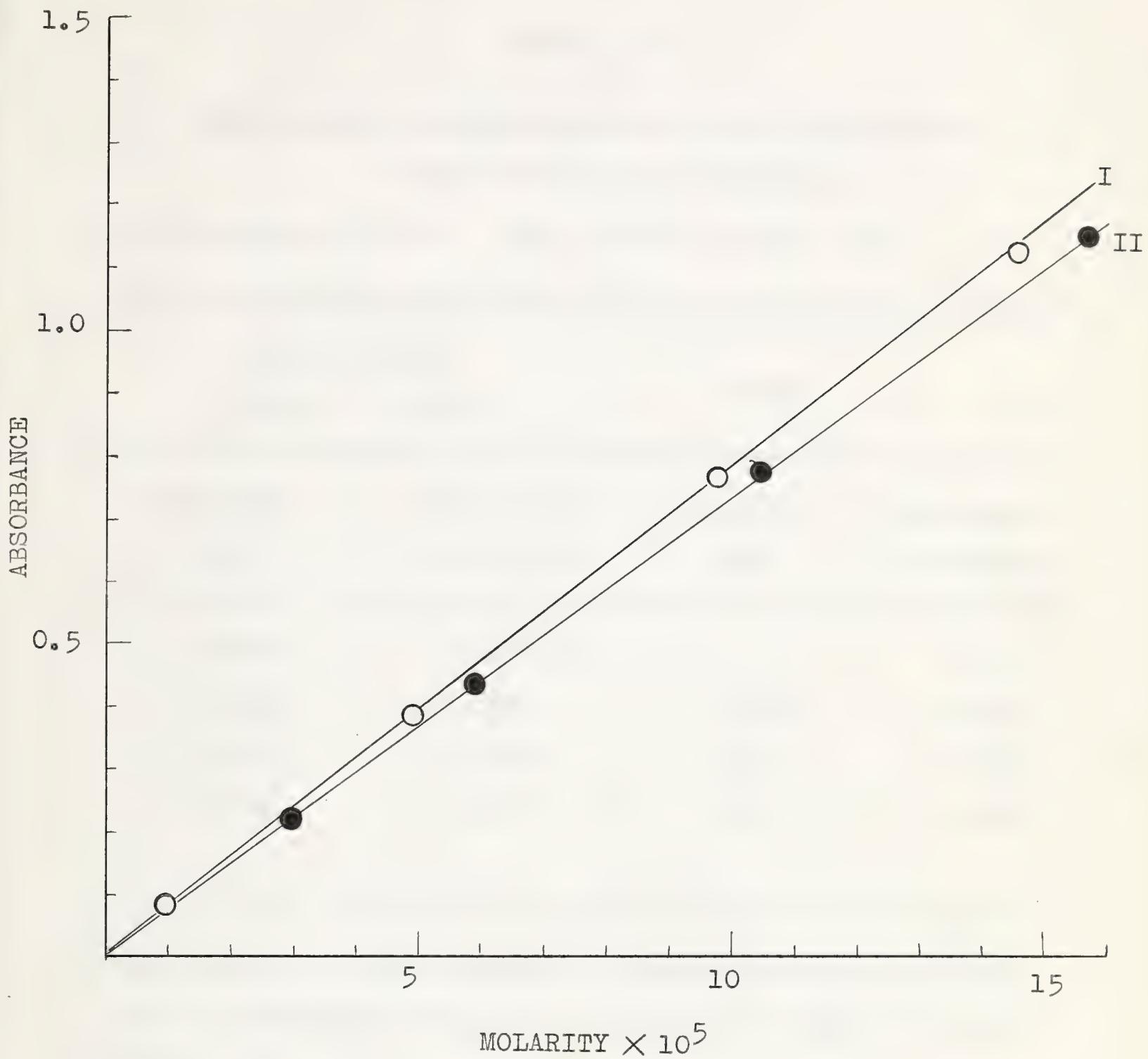


Fig. 18. Beer's law plots at 25°C for nitrobenzene solutions
● in water at 267 m μ , ○ in 40% by weight ethanol in water
at 265 m μ .

TABLE 19

Relationship between Absorbance and Concentration
for Nitrobenzene Solutions

Readings made at 25°C. Data plotted in Fig. 18.

40% by weight ethanol in water		Water	
Molarity $\times 10^5$	Absorbance at 265 μ	Molarity $\times 10^5$	Absorbance at 267 μ
0.97	0.078	2.96	0.220
4.85	0.380	5.92	0.434
9.71	0.760	10.4	0.765
14.50	1.120	15.6	1.150

From Fig. 18. Molar extinction coefficients of 7760 and 7340 are obtained for aqueous-ethanol and water solutions respectively.

The stock solution of sodium sulphide was prepared by the addition of sufficient $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (neglecting the change in the water concentration due to the water of hydration) to the 40% aqueous ethanol to make the solution 0.960 molar with respect to the Na_2S . This stock solution was then diluted appropriately with the 40% aqueous ethanol in the preparation of a 0.160 M solution of sodium sulphide. A 0.160 M solution of sodium sulphide made in this manner contained 61.2% of water and 38.8% of ethanol. The concentrations referred to were for 50.0°C.

The solutions were prepared at 25°C and the weight of sodium sulphide required at that temperature multiplied by a factor of 1.0210 was taken. The value of 1.0210 is the ratio of the specific gravities of the solvent (38.8% by weight ethanol in water) at 25°C and at 50°C as obtained from the values given in the International Critical Tables (98).

The absorbances of the resultant solutions were measured at 450 μu taking the usual precautions to exclude air. The measurements were obtained at room temperature (25°C) and also at 50.0°C. The results for the sodium sulphide solutions of sulphur in aqueous ethanol are recorded in Table 20 and plotted in Fig. 19. The corresponding results for the aqueous sodium sulphide-ammonium chloride solutions appear in Table 21 and are plotted in Fig. 20.

One milliliter aliquots of the sodium sulphide solutions of sulphur in aqueous ethanol were diluted 100-fold by aqueous ethanol which was approximately 0.005 M in hydrochloric acid. The absorbance of each resultant solution was then measured at 265 μu and is recorded in Table 22 with the corresponding

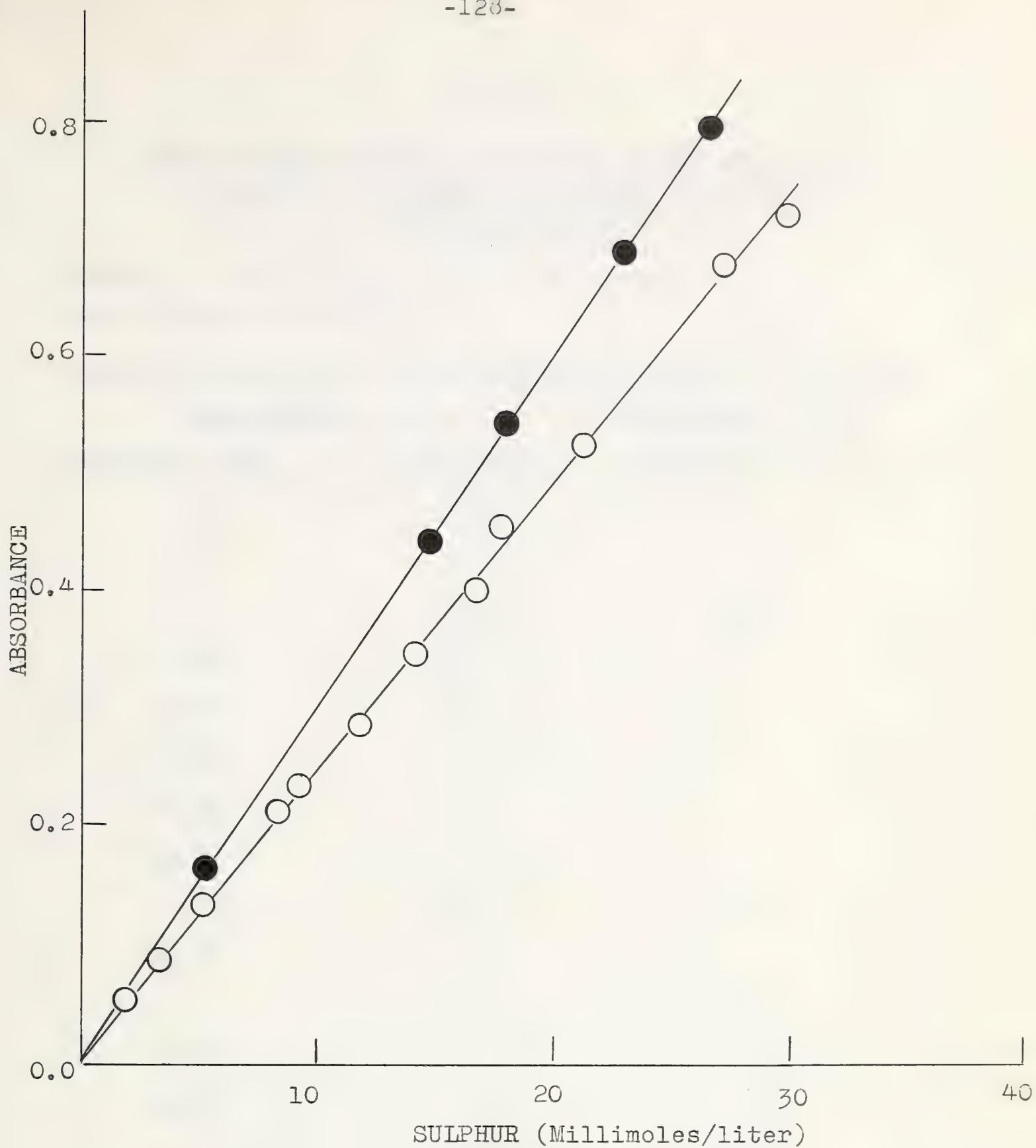


Fig. 19. A plot of the concentration of sulphur dissolved in 0.160 M Na_2S in aqueous ethanol vs. the absorbance of disulphide at 450 $\text{m}\mu$ at 25°C, O, and at 50°C, ●.

TABLE 20

Relationship between Absorbance at 450 m μ and the
Molarity of Sulphur Dissolved in 0.160 M
Sodium Sulphide

Solvent, 40% by weight ethanol in water.

Data plotted in Fig. 19.

<u>Molarity</u> $\times 10^3$	<u>Temperature, 25°C</u>	<u>Temperature, 50°C</u>
	Absorbance	Absorbance*
3.34	0.088	
5.01	0.132	
	0.136	0.166
6.68	0.190	
8.35	0.212	
9.20	0.236	
10.90	0.280	
14.20	0.345	
	0.360	0.440
16.70	0.400	
	0.441	0.540
17.80	0.452	
21.40	0.520	
	0.560	0.685
	0.650	0.793
27.30	0.677	
30.00	0.719	

* Corresponding molarity not determined.

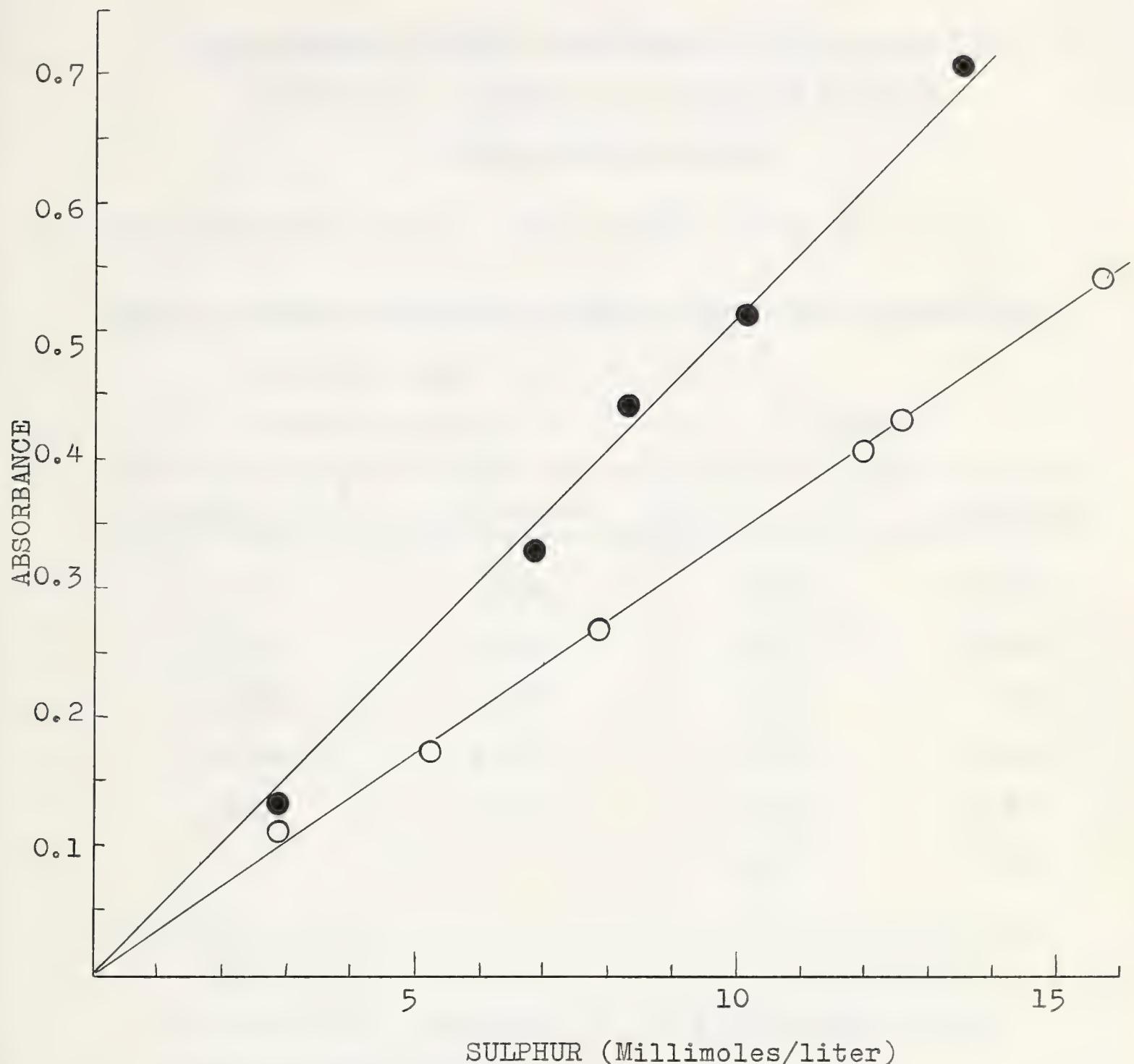


Fig. 20. A plot of the concentration of sulphur dissolved in 0.150 M Na_2S vs. the absorbance at 450 m μ at 50.0°C. ● in 40% by weight ethanol in water and ○ in water alone.

TABLE 21

Relationship between Absorbance at 450 mu and the
Molarity of Sulphur Dissolved in 0.150 M
Sodium Hydrosulphide

Data obtained at 50.0°C and plotted in Fig. 20.

40% by weight

ethanol in water		Water	
Molarity $\times 10^3$	Absorbance	Molarity $\times 10^3$	Absorbance
2.75	0.130	2.84	0.108
6.81	0.330	5.21	0.178
8.25	0.445	7.81	0.270
10.04	0.515	11.90	0.410
13.36	0.710	12.50	0.437
		15.60	0.545

The blank cell contained 0.150 M hydrosulphide ion
with no added sulphur

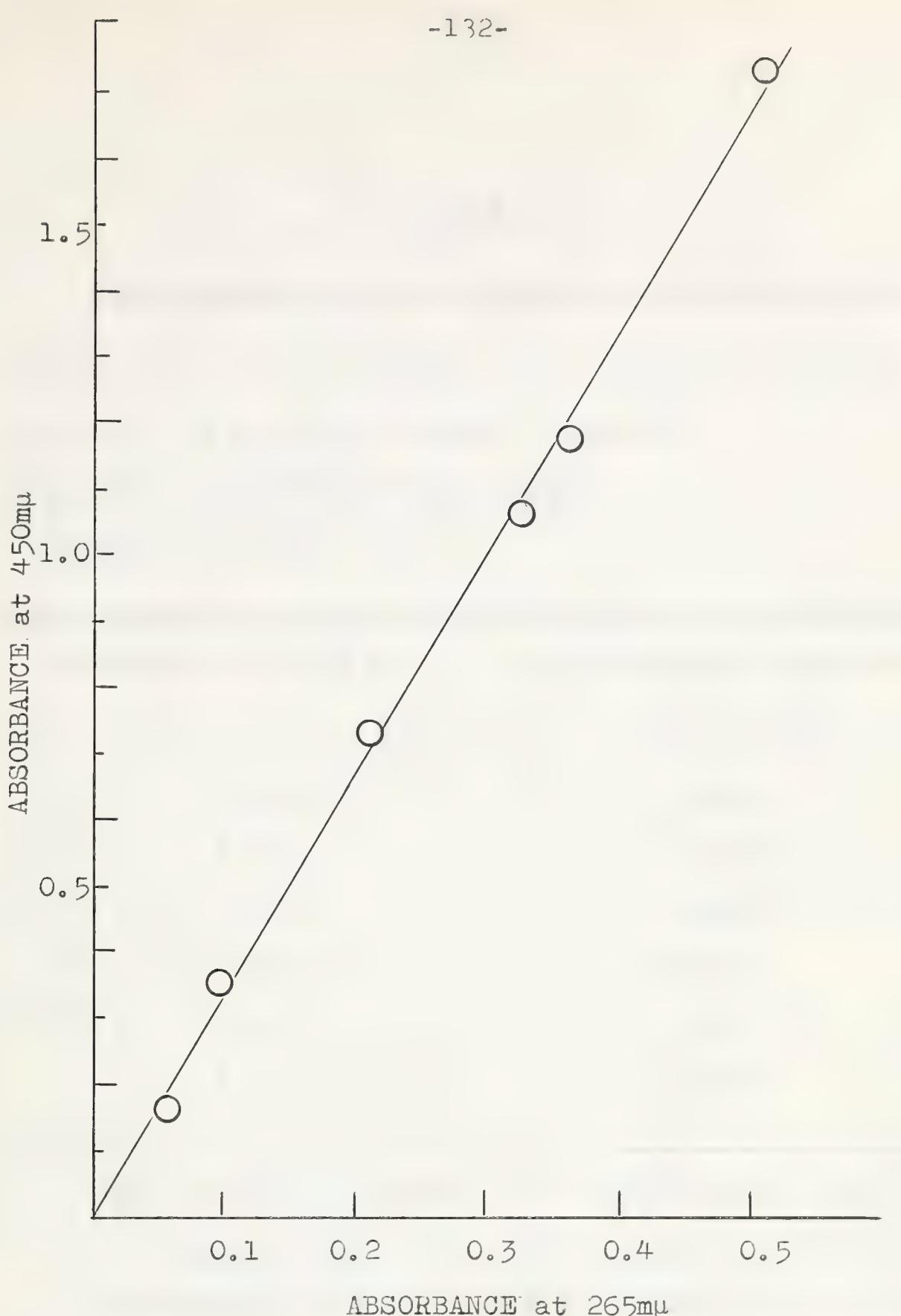


Fig. 21. The absorbance at $450\text{ m}\mu$ of solutions of sulphur in $0.160\text{ M Na}_2\text{S}$ vs. the corresponding absorbance at $265\text{ m}\mu$ after 100-fold dilution and acidification with a standard aqueous ethanolic solution of HCl. All absorbances measured at 25°C .

TABLE 22

Calibration of Interference Due to Sulphur at 265 mu

Molarity of sodium sulphide before dilution, 0.160 M.

Solvent, 40% by weight ethanol in water.

Absorbance measurements made at 25°C

Data plotted in Fig. 21.

Absorbance at 450 mu	Corresponding absorbance at 265 mu*
0.160	0.065
0.350	0.098
0.728	0.213
1.060	0.325
1.170	0.361
1.735	0.510

* After 100-fold dilution and acidification (see text)

The blank cell for both sets of readings contained the corresponding sodium sulphide solution with no added sulphur.

absorbance at $450\mu\text{u}$ before dilution. The plot in Fig. 21 relating these two absorbances gives a factor of 0.294 for absorbance at $265\mu\text{u}$ after dilution divided by the absorbance at $450\mu\text{u}$ (25°C) before dilution. The corresponding factor for the absorbance at $450\mu\text{u}$ at 50.0°C is 0.240. This latter factor has been used to determine interference due to sulphur in measurements at $265\mu\text{u}$ for nitrobenzene.

Typical calculation for interference at $265\mu\text{u}$ due to sulphur

From Figs. 19 and 21 the following relationship is obtained for sodium polysulphide solutions in 40% (by weight) ethanol in water.

$$\begin{aligned} & \text{Absorbance at } 450\mu\text{u} (50^{\circ}\text{C}) \times 0.240 \\ \equiv & \text{Absorbance at } 265\mu\text{u} \text{ after acidification} \\ & \text{and 100-fold dilution at } 25^{\circ}\text{C}. \end{aligned}$$

The factor of 0.240 was used to correct for sulphur interference in Figs. 2 and 4. The corresponding absorbance at $450\mu\text{u}$ in each case was obtained from Figs. 3 and 5.

Example

$$\begin{aligned} \text{Observed absorbance at } 265\mu\text{u} & \equiv 1.190 \\ \text{Corresponding absorbance at } 450\mu\text{u} & \equiv 0.235 \\ \text{Sulphur absorbance at } 265\mu\text{u} & \equiv 0.235 \times 0.240 \\ & \equiv 0.057 \\ \text{Nitrobenzene absorbance at } 265\mu\text{u} & \equiv 1.190 - 0.057 \\ & \equiv 1.133 \end{aligned}$$

When sodium hydroxide was added (as in Figs. 4 and 5) the observed absorbance at $450\mu\text{u}$ was first divided by a correction factor obtained from Fig. 1 before applying the above treatment. These factors are given below.

<u>Molarity of NaOH</u>	<u>Correction factor</u>
0.160	1.10
0.320	1.20
0.800	1.35
1.600	1.50

The stock solution of sodium sulphide - ammonium chloride was obtained by first preparing a 0.900 M solution of sodium sulphide in deaerated, distilled water. This was placed in a flask equipped with a stirrer, and the surface of the solution was blanketed by a stream of nitrogen. The electrodes for the pH measurement were immersed in the liquid and solid ammonium chloride was added in portions, while rapid stirring was maintained. The addition of solid ammonium chloride was continued until the pH had been reduced to 10.5 at 25°C , giving a solution 0.944 M in ammonium chloride.

The resultant solution was then forced out through a porous disc, under nitrogen pressure, into the reservoir flask. This flask and the whole system used in the reduction experiments had previously been flushed out with nitrogen.

Preparation of Polysulphide Solutions

The procedure adopted for the preparation of these solutions was essentially the same for aqueous ethanolic sodium sulphide as for aqueous sodium sulphide - ammonium chloride. Sulphur was added to a weighed Erlenmeyer flask fitted with a ground glass stopper and provided with a magnetic stirring bar. After the flask was weighed, the air in the flask was displaced by a gentle stream of nitrogen, and an aliquot of the sulphide or

hydrosulphide solution (usually 50 mls) added. With the flask securely stoppered, (the stopper being well greased) the mixture was then rapidly stirred at room temperature until dissolution of the sulphur was complete. In the case of ethanolic sodium sulphide this was usually accomplished within one hour. The aqueous hydrosulphide, however, had to be left stirring overnight in order to completely dissolve the sulphur.

The solutions required for the comparative absorption of disulphide and hydrodisulphide ions were made up as follows. All preparations were carried out in an atmosphere of nitrogen. To the stock solution of 0.960 M sodium sulphide was added the requisite amount of elemental sulphur. Ten-milliliter aliquots of the resulting solution were separately treated with base, acid, or bicarbonate as required and subsequently diluted to 60 ml with the 40% aqueous ethanol. The aliquot which was to supply the solution of disulphide was first basified by addition of the necessary amount of solid sodium hydroxide to give a concentration of added base equal to 4 M and then the volume made up to 60 ml. One of the aliquots which was to supply the solution of hydrodisulphide was acidified by slowly adding the requisite quantity of constant-boiling hydrochloric acid to the rapidly stirred solution. The pH of the solution was followed during this addition and found to be 10.7 when all the necessary hydrochloric acid had been added. To the other aliquot was added an equimolar quantity of solid sodium bicarbonate in an attempt to convert all the sodium sulphide and sodium disulphide to the corresponding hydrosulphide and hydrodisulphide (61) and then the volume made up to 60 ml. This solution was cooled to 0°C and the sodium

carbonate allowed to precipitate. The supernatant solution of sodium hydrosulphide and sodium hydrodisulphide (pH = 10.7) was removed from the flask, under nitrogen pressure, through a porous plate.

The solutions of sodium hydrosulphide, and sodium hydrosulphide containing hydrodisulphide, were prepared from the 0.960 M sodium sulphide stock solution, by appropriate addition of elemental sulphur in the latter case, and then suitable acidification with hydrochloric acid during the dilution, to give the final concentration of 0.160 mole per liter.

SECTION 3

Part II

Apparatus and Procedure Employed in the Rate Determinations

A. Apparatus

A Beckman Model DU spectrophotometer, equipped with a power pack, was used to make the absorption measurements. Matched, glass-stoppered quartz cells of 10-mm light path were used for all measurements.

The cell compartment was thermostatted with the Beckman double thermospacer unit. By providing this with an asbestos-coated wooden lid, it was found that, once thermal equilibrium had been attained, the temperature of the cell contents could be maintained at $50.00 \pm 0.03^{\circ}\text{C}$. This was determined by taking periodic thermometer readings during the course of several typical reductions.

The thermometers of both thermostat baths were checked against a thermometer calibrated by the National Bureau of Standards. No correction for 50.0°C was found to be necessary.

The pH determinations were made with a Beckman Zeromatic meter equipped with a high pH electrode. The standardization was made with a saturated solution of calcium hydroxide (Fisher "certified" reagent), purified by leaching five times with distilled water. This has a pH of 12.45 at 25°C (99). Standard buffers were used at lower pH.

The reductions were carried out in a 500-ml, four-necked flask fitted with an efficient, water-cooled reflux condenser, a stirrer with an air-tight seal, an inlet for the addition of sodium sulphide solutions, and an inlet for a nitrogen bleed. In addition, a tube dipping below the surface of the solutions held a 1-ml pipette.

thus permitted sampling so that there was a minimum of exposure of the solution surface to air. The apparatus was thermostatted at 50.0° C. A calibrated dropping funnel was used to introduce the solution of sodium sulphide into the reaction vessel. The funnel was connected to a darkened two liter flask which contained the stock solution of the reducing agent. A system of connecting tubes with suitable stopcocks was used, which allowed transference of stock solutions (including the deaerated solvents) from their storage flasks to the reaction vessel (via the funnel) under nitrogen pressure.

B. Procedure

The reaction vessel was first flushed with nitrogen and subsequently a slight positive pressure of nitrogen was maintained in the apparatus above the solution throughout the entire reaction period. The nitrogen was passed through alkaline pyrogallol solution before use.

Sodium sulphide reductions

About 50 ml of the stock solution (0.960 M sodium sulphide in aqueous ethanol) was added to the reaction vessel, followed by a sufficient volume of the mixed solvent to give a final concentration of 0.160 M sodium sulphide. For the cases which required the addition of sodium hydroxide or elemental sulphur, the necessary quantity of the reagent was added before the diluting solvent had been completely added, followed by the remainder of the solvent needed to make up the required volume. The solutions made by the addition of sodium hydroxide or sulphur were allowed to stand for one-half hour to ensure equilibration of the species in the solution. No change in absorption ($>\pm 1\%$) was noted in such an equilibrated solution, even upon prolonged standing. Finally, the nitrobenzene was introduced, by means of

a Victor Meyer bottle, into the rapidly stirred solution.

For following the change in absorption at 450 μ , the Beckman DU cell container was thermostatted at 50.0°C. The glass-stoppered cell, previously flushed with nitrogen, was completely filled with freshly prepared initial reaction solution obtained from the reaction flask and the change in absorbance was measured continuously and directly. This eliminated errors due to cooling and air oxidation which would occur if fresh samples were taken periodically from the reaction flask.

To follow the change in nitrobenzene concentration, 1-ml samples were withdrawn from time to time and immediately diluted to 100 ml with a standard mixture of 40% aqueous ethanol containing four times the calculated amount of hydrochloric acid required to convert all the sodium sulphide to H_2S and the amine to the hydrochloride. These solutions, properly protected and capped, were allowed to stand for the duration of the experiment (2-4 hours) before measurements were made, and then the absorbances were obtained at 25°C at 265 μ . The period of standing produced no alteration in absorption and thus permitted the choice of a more convenient time for the absorption measurements. Interfering absorption at 265 μ due to polysulphide was subtracted from the total absorption at this wave length to give a measure of the nitrobenzene concentration. The magnitude of this interfering absorption due to polysulphide was evaluated as outlined in Part IB of this section.

The sodium sulphide-ammonium chloride reductions

The reductions were carried out using essentially the same apparatus and procedure as in the previous work with sodium

monosulphide. The reflux condenser was dispensed with, however, as in trial experiments it was found that considerable condensation of hydrogen disulphide took place there,¹ followed by decomposition and deposition of sulphur. The reaction mixture was at all times blanketed by nitrogen which had been passed through alkaline pyrogallol. Two hundred and fifty ml of an aqueous solution of nitrobenzene was pipetted into the reaction vessel and allowed to reach the thermostatted bath temperature ($50.00 \pm 0.03^\circ\text{C}$). Then 50 ml of a 0.900 M sodium sulphide-ammonium chloride solution, first brought to 50° in a jacketted vessel, was introduced from an automatic pipette. The solution was thus 0.150 molar with respect to hydrosulphide and 0.015 molar or less in nitrobenzene. Time measurements were begun when all this solution had been added.

For spectrophotometric measurements of polysulphide in the visible region at $450 \text{ m}\mu$, a portion of the reaction mixture was transferred by means of a warmed pipette to a glass-stoppered sample cell in the thermostatted cell compartment of a Beckman DU spectrophotometer. The glass cell, previously flushed with a stream of nitrogen was filled completely with the solution so that no space was left between the solution surface and the stopper.

¹ The yellow condensate was presumed to be hydrogen disulphide. This had been prepared by the distillation of acidified sodium disulphide (100), and probably arose from the hydrolysis of hydrodisulphide ion in this work.



The condensate was soluble in ethanol, but addition of water caused decomposition to a yellow solid. The solid burned with a blue flame, giving the characteristic odor of sulphur dioxide.

It was important that the stopper fitted well (a small quantity of Apiezon grease was used) in order to exclude atmospheric oxygen and to prevent loss of H_2S and other volatile components of the reaction solution. That these solutions were in fact unaffected by air oxidation was borne out by the fact that under these conditions polysulphide solutions could be kept for two or three days with no noticeable decrease in absorbance (i.e. $>\pm 1\%$).

The spectrophotometric method previously used for estimating the nitrobenzene concentration was modified so that the 1 ml samples removed from the reaction mixture at timed intervals were diluted to 200 ml with 0.002 M aqueous hydrochloric acid. This procedure effectively "froze" the reaction and caused any polysulphide to be precipitated as sulphur leaving a residual "blank" absorbance due to the inorganic components. This blank was found to be constant for the course of the reaction. However, as the precipitated sulphur appeared in a very finely divided form it was necessary to allow the diluted sample to stand for 24 hours before the sulphur settled completely and absorption measurements at 267 m μ were made.

Reduction of the para-alkyl nitrobenzenes

The same apparatus and procedure used for the sodium sulphide-ammonium chloride reduction of aqueous nitrobenzene was employed here. Two hundred milliliters (at 25° C) of 95% ethanol was introduced into the flask with 50 ml of a 0.1500 M solution (at 25° C) of the nitrobenzene solution in 95% ethanol. When this solution had reached 50° C the 50 ml of stock aqueous sodium sulphide solution was added with rapid stirring. Some of

the solution was then quickly transferred to the spectrophotometer cell, taking all the precautions outlined previously. Only readings at 450 m μ were taken. All attempts to make readings in the ultra-violet region were unsatisfactory. Apparently the ethanol present prevented the precipitation of sulphur in the normal acidification-dilution technique and thus gave rise to interference in the absorbance measurements.

SECTION 3

EXPERIMENTAL

Part III

Determination and Isolation of Organic Reaction Products

A. The sodium sulphide reductions

(1) Nitrobenzene

In order to simplify the extraction procedure, the quantities of reactants used in the reduction were increased, although still keeping a large excess of sodium sulphide over nitrobenzene. Nitrobenzene (12.30 gm.) was dissolved in one liter of aqueous ethanol (40% by weight ethanol) containing 120 gm. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. The reaction mixture was maintained at 50°C for five hours in a stoppered one-liter flask. The solution was then evaporated under reduced pressure at 50°C to remove the ethanol. The remaining mixture, after dilution with 200 ml. of water, was extracted three times with ether and the combined extracts evaporated to dryness. The resultant oil was completely soluble in hydrochloric acid, the solution providing 12 gm. (90%) of aniline hydrochloride, m.p. 198°C (lit., (60) 198°C).

(2) p-Nitrotoluene

Using 13.7 gm. (0.1 mole) of p-nitrotoluene and the same procedure as outlined for nitrobenzene, 10.14 gm. (97%) of crude p-toluidine were obtained m.p. $39^\circ - 42^\circ\text{C}$. Acidification with concentrated hydrochloric acid produced an intensely red solution, which on extraction with ether left a colourless aqueous layer. Basification of the aqueous layer gave 9.0 gm. of p-toluidine, which after sublimation, had a m.p. of 44°C . The ether

extract provided only 0.2 gm of an infusible, amorphous red solid which was not steam distillable (40).

B. Sodium sulphide-ammonium chloride reductions of p-nitrotoluene and p-nitro-t-butylbenzene

From typical reduction mixtures of each, a 100 ml aliquot of the solution was removed after a reaction period of about 12 hours. These were evaporated at 50° C on a rotary evaporator until an oil separated. The oily amine was extracted with ether and the ether extract dried over anhydrous sodium sulphate. Evaporation of the extract to dryness, gave the amine in each case. Acidification of this material obtained from the p-nitrotoluene reduction gave no red colour, indicating the absence of any p-aminobenzaldehyde. Moreover this solid was completely soluble in acid. The p-toluidine, m.p. 44° C, gave 30mg of the hydrochloride corresponding to a 75% recovery. The crude p-amino-t-butylbenzene was obtained as an oil. Yield, 30 mg, 80% recovery. In order to characterize this amine, it was prepared independently by refluxing an ethanolic solution of p-nitro-t-butylbenzene with a three-fold excess of stannous chloride and hydrochloric acid for one hour. The solution was evaporated to dryness, basified with sodium hydroxide solution and extracted with ether. The ether extract, after drying over anhydrous sodium sulphate, was evaporated, leaving the amine as a yellow-brown oil. N-(p-t-butylphenyl)-p-tolylsulphonamide was prepared from the two samples of the amine by tosylation (101). After recrystallization of the derivatives from ethanol, both melted at 175° C. A mixed melting point carried out on the two substances gave no depression of melting point. Furthermore, their infrared spectra were identical.

The infra-red spectrum obtained from a film of the amine exhibited strong N-H absorbance at 3450 cm^{-1} and at 3370 cm^{-1} (102).

C. Sodium sulphide-ammonium chloride reduction of nitrobenzene

From a typical reduction mixture initially 0.01 M in nitrobenzene and 0.150 M in hydrosulphide ion, a 100-ml aliquot was removed after an 18-hour reaction period. This solution was extracted with three portions of ether, totalling about 50-ml. The ether extract was shaken with one ml of concentrated hydrochloric acid and the two liquid layers separated. The ether layer on evaporation to dryness left no residue. The acid extraction on careful evaporation to dryness gave 75 mg of aniline hydrochloride as an almost white, crystalline solid, m.p. 198°C ; Lit. 198°C (60). This represents about a 60% recovery of the amine based on the initial nitrobenzene concentration, and considering the small quantities involved is probably as high as can be expected.

D. Utility of vapor phase chromatography.

A Burrell Kromotog K-2 was used for all V.P.C. analyses. A 2.5-meter column, containing a celite support coated with 20% of its weight of silicone rubber, at a temperature of 210°C with a helium flow rate of 70 ml/min, gave good separation of a known mixture of aniline, phenylhydroxylamine and nitrobenzene (See Fig. 22).

At elevated temperatures (120°) phenylhydroxylamine is known to decompose into products, two of which are believed to be aniline and azoxybenzene (103). Under the present conditions, authentic azoxybenzene showed no retention band on the chart, whereas phenylhydroxylamine gave two peaks of retention time 135 and 180 seconds.

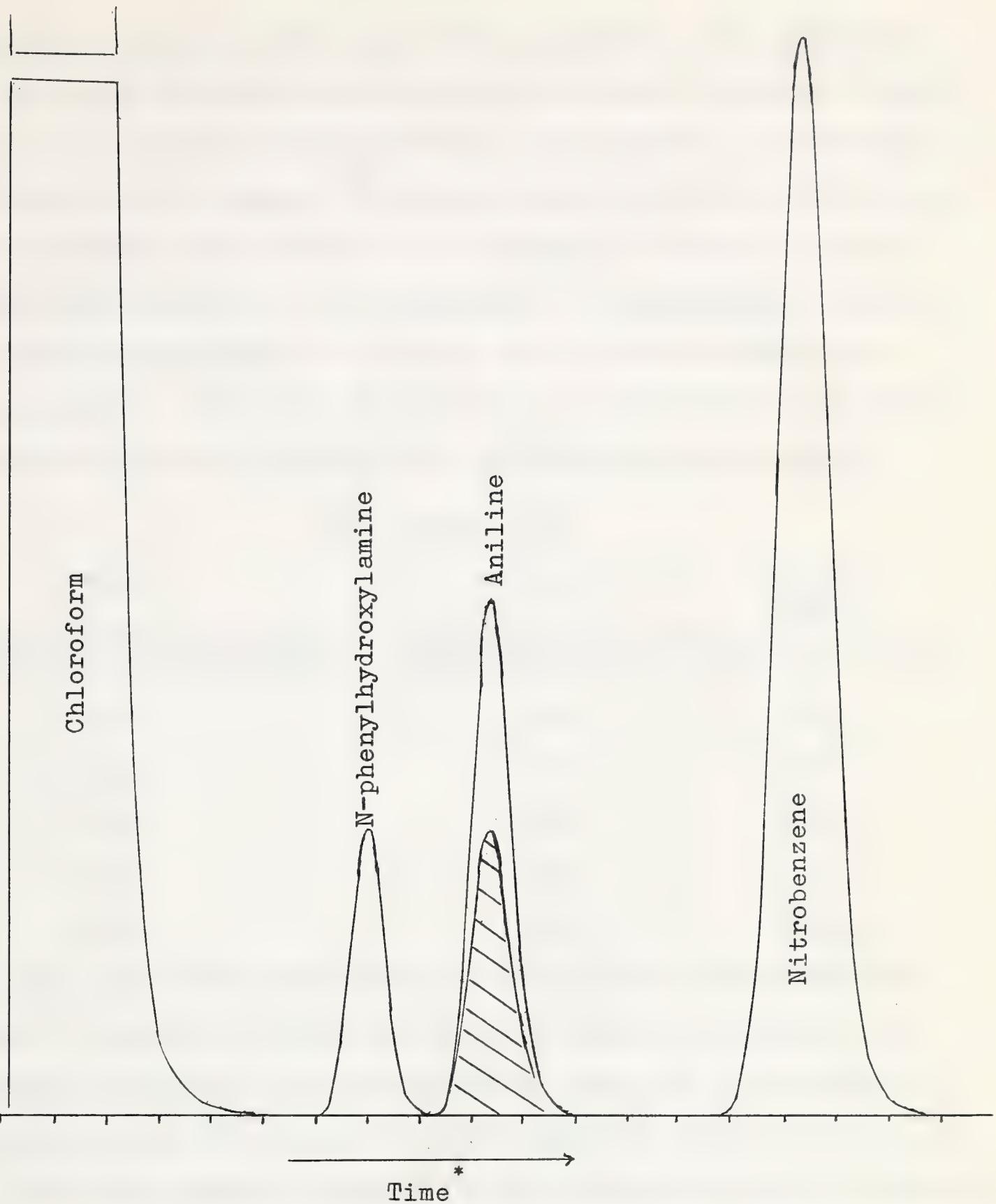


Fig. 22. The vapour phase chromatogram of a synthetic mixture of N-phenylhydroxylamine, aniline and nitrobenzene in chloroform. The shaded area in the aniline peak approximately represents the aniline produced from phenylhydroxylamine decomposition. Column conditions as per p.146.

*Marked in 15 second divisions.

The second band was shown to be due to aniline. The identity of the first band was not established although it may have been due to the unchanged hydroxylamine. The important observation made was that the ratio of these two peaks under the conditions of this analysis was found to be constant at a value of second peak/first peak=1.13±0.03, regardless of the original quantity of phenylhydroxylamine, or solvent used, or the presence of nitrobenzene. The value of the ratio of 1.13±0.03 is the average value obtained from the five following determinations.

<u>Peak areas (Cm²)</u>		
Peak 1	Peak 2	Peak 2 Peak 1
Retention time 135 secs.	Retention time 180 secs.	
0.78	0.87	1.12
2.28	2.52	1.10
2.53	2.94	1.16
3.53	4.07	1.15
3.70	4.20	1.12

By calibration with authentic aniline and phenylhydroxylamine it was thus possible to analyse mixtures of aniline and phenylhydroxylamine by first measuring the area of the peak of retention time 135 seconds and multiplying it by the factor 1.13 to obtain the area of the peak for the aniline produced by phenylhydroxylamine's decompostion during the analysis. The difference between this calculated area and the actual area was due to additional aniline present with the phenylhydroxylamine before the V.P.C. determination. The analysis of several such synthetic mixtures did show dearly the presence of as little as 5% aniline

originally present. Although this analysis was not highly accurate it did show qualitatively the presence or absence of phenylhydroxylamine and aniline as reduction products. This analysis was used in conjunction with infrared analyses for OH stretching at 3580 cm^{-1} and 3700 cm^{-1} due to phenylhydroxylamine (102)

A typical calculation to determine relative quantities of aniline and phenylhydroxylamine

The example considered is for the results obtained from the reduction of 0.010 M phenylhydroxylamine by 0.150 M hydrosulphide carried on for 50 hours.

Calibration factor of aniline peak $= 2.26 \times 10^{-7}$ moles/ sq. cm. Calibration factor of the 135 second retention time peak due to phenylhydroxylamine $= 5.90 \times 10^{-7}$ moles/sq. cm. (Note: Both these factors were obtained as average values of three separate passes)

Results Area of first peak = 1.09 sq. cms.

 Area of second peak = 10.4 sq. cms.

Thus area of that portion of the second peak due to phenylhydroxylamine $= 1.09 \times 1.13 = 1.23$ sq. cms.

Therefore area of second peak due only to aniline $10.4 - 1.23 = 9.2$ sq. cms. which when multiplied by the calibration factor gives a value of 2.1×10^{-6} moles. From the area of the first peak, the number of moles of phenylhydroxylamine remaining $= 1.09 \times 5.9 \times 10^{-7}$
 $= 6.4 \times 10^{-7}$ moles

Therefore the percentage of the original phenylhydroxylamine reduced to aniline $= 75\%$.

Analysis of the reaction mixture after 60 minutes reduction time

The practically colourless mixture, 0.010 M in nitrobenzene

and 0.150 M in hydrosulphide, was allowed to react. A slow development of yellow colour (measurable at 450 μ) due to hydrodisulphide occurred. After 60 minutes of reaction a 100-ml aliquot was extracted with ether, the ether extract dried ($MgSO_4$) and then freed of solvent. The residue was taken up in chloroform. Analysis by V.P.C. indicated the presence of very little aniline, approximately 1-2%, but much phenylhydroxylamine as well as unchanged nitrobenzene. Strong absorption in the infrared characteristic of phenylhydroxylamine corroborated these results.

Analysis of the reaction mixture after 18 hours reduction time

A 100-ml aliquot of the above yellow reaction mixture, removed after 18 hours of reaction, when treated as above showed by V.P.C. analysis the presence only of aniline along with a small amount of unchanged nitrobenzene. No absorption in the infrared region due to phenylhydroxylamine could be detected.

Other organic reduction products of nitrobenzene

A carbon tetrachloride solution of the extracted reduction products, taken at intervals during the course of the reaction, was at all times colourless. Measurements at the λ_{max} at which azoxybenzene, and azobenzene absorb showed no increase in absorption, thus demonstrating that bimolecular reduction products were absent.

Phenylhydroxylamine reduction by hydrosulphide

An aqueous solution, 0.01 M in phenylhydroxylamine and 0.150 M in hydrosulphide, was allowed to react at 50°. No development of yellow colour due to hydrodisulphide occurred throughout the course of reduction. A 100-ml aliquot was removed

after 50 min. of reaction time and analyzed. V.P.C. showed no significant formation of aniline, thus indicating no significant reduction during this time. The same results were obtained from an aliquot removed after 90 minutes of reaction.

After a 24-hour reaction period however, a considerable amount of aniline had been produced, indicating that a slow reaction did occur between phenylhydroxylamine and sodium hydro-sulphide.

Phenylhydroxylamine reduction by hydrodisulphide

An aqueous solution was prepared 0.01 molar in phenylhydroxylamine and 0.150 molar with respect to hydrosulphide ion, containing enough elemental sulphur predissolved in the sodium hydrosulphide solution to convert about 7 to 8 per cent of the hydrosulphide to hydrodisulphide. The concentration of hydrodisulphide was measured by reference to a Beers' law plot of absorption at 450 m μ versus concentration of sulphur in aqueous 0.150 molar sodium hydrosulphide (see Fig. 20)

A continual decrease in absorption at 450 m μ occurred as reduction progressed. An aliquot removed after 70 min. of reaction indicated by V.P.C. analysis that about 30% of the phenylhydroxylamine had been converted to aniline. After 1000 minutes of reaction approximately 90% of the hydroxylamine had become aniline.

SECTION 3

EXPERIMENTAL

Part IV

Determination of Thiosulphate Ion and Sulphide Ion

The iodometric titrations for thiosulphate and sulphide ions employed in this work were carried out by standard procedures (63). Pure iodine was used as the primary standard.

A. Thiosulphate determination in the reduction of nitrobenzene by sodium sulphide in aqueous ethanol

A typical reduction mixture (0.160 M in sodium sulphide and 0.0150 M in nitrobenzene) containing no dissolved sulphur was maintained at 50°C for 24 hours. A 100-ml aliquot of the solution was then removed and added to a suspension of freshly precipitated cadmium carbonate. The latter was prepared from equimolar quantities of sodium carbonate and cadmium sulphate. A two-fold excess of the cadmium carbonate based on the original sodium sulphide concentration was employed. The resultant suspension was stirred vigorously for 30 minutes by which time the odour of hydrogen sulphide was no longer evident. The whole suspension was then transferred to a rotary evaporator and evaporated at 50°C under reduced pressure almost to dryness. Considerable "bumping" took place even under these conditions. The resultant mixture was shaken vigorously with 200 ml of water, filtered and the remaining solid material washed twice with water. Titration of this solution with iodine using a starch indicator gave a thiosulphate ion concentration in the reduction solution of 0.004 M.

B. Thiosulphate determinations in the reduction of nitrobenzene by aqueous sodium sulphide-ammonium chloride

The estimation of thiosulphate ion concentration formed by the reduction of nitrobenzene with 0.150 M sodium sulphide-ammonium chloride in aqueous solution was first carried out by using cadmium sulphate as a precipitant for sulphide and polysulphide ion. However, it was found that co-precipitation of thiosulphate under these conditions was even more extensive than that observed in the ethanolic sodium sulphide system. In fact, using only small aliquots (15 ml) of the final reaction mixture, practically no thiosulphate was detectable. When 100-ml aliquots were taken the apparent thiosulphate concentration was approximately 0.001 M in the final reduction solution. However, as the conditions of this particular reduction, viz. aqueous solution and relatively low pH, presented no difficulties in the use of cadmium carbonate as a precipitating agent, it was decided to determine thiosulphate concentration using this reagent.

An excess of a freshly prepared suspension of cadmium carbonate was used to precipitate sulphide and di (or poly) sulphide from a 100 ml aliquot of the reaction mixture. It was found necessary to remove the organic material (chiefly aniline) from the aliquot of the reaction mixture by ether extraction prior to the treatment with cadmium carbonate. If this was not done, complete precipitation of sulphide and disulphide could be brought about only by repeated treatments with cadmium carbonate. Moreover, the filtrations involved were hampered by the tendency of the precipitate to clog the porous plate of the filter, thus making the procedure quite time-consuming. By prior removal of

* However, addition of ammonium chloride reduced the pH to a value less than 8 and permitted satisfactory titration of thiosulphate with 0.0500 N iodine to a starch end point.

the aniline it was possible to obtain complete precipitation of the sulphide species by only one application of cadmium carbonate suspension, vigorously stirred with the aliquot for 10 minutes. Following the removal of all precipitate by filtration, it was found that the pH of the resultant solution was above 9, due to the presence of sodium carbonate. This base interfered in the titration with iodine by giving an indefinite end point. ^{Additional} ←

The procedure outlined above, when applied to synthetic mixtures of known amounts of sodium sulphide-ammonium chloride and sodium thiosulphate, gave quantitative recovery of the thiosulphate.

Cadmium carbonate freshly precipitated from an equimolar mixture of cadmium sulphate and sodium carbonate also proved to be very satisfactory as a precipitant for sulphide and polysulphide ions. However as this modification provided no marked improvement of the precipitation process it was not adopted for general use in this work.

C. Estimation of initial thiosulphate and sulphide ion concentrations in the reaction solutions

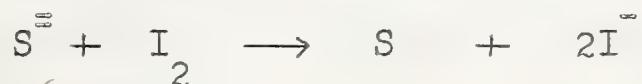
Thiosulphate

This was determined in the 0.900 M sodium sulphide-ammonium chloride solution by the same procedure as outlined above. A thiosulphate ion concentration of 0.0210 M was indicated corresponding to 0.0035 M in the 0.150 M sodium sulphide-ammonium chloride solutions used in this work.

Sulphide (63)

This determination was carried out on the original sodium

sulphide crystals $\text{Na}_2\text{S}_{2,9}\text{H}_2\text{O}$. Crystals of the sulphide were taken, wiped free from adhering moisture, weighed and dissolved in sufficient water to give a solution less than 0.01 M in sulphide ion. This was immediately titrated with 0.0251 M iodine solution, using a starch indicator. Excellent end-points were obtained and were found to be repeatable. Thus two separate titrations indicated that 0.1000 gm of the sulphide required 16.70 ml of 0.0251 M iodine solution. However from the results for thiosulphate determination above it is evident that some of the iodine is accounted for by the contaminating thiosulphate. The above values indicate that 0.20 ml of the iodine solution is due to the thiosulphate. Thus the sulphide ion in 0.1000 gm of the nonahydrate accounted for 16.50 ml of iodine solution which corresponds to 0.00415 mole of sodium sulphide on the basis of the reaction stoichiometry as expressed by



The theoretical number of moles is $0.1000/240.2 = 0.00416$. Thus the sodium sulphide used contained 99.8% of the theoretical sulphide ion content.

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Possible Mechanisms for the Reduction of Nitrobenzene
and Phenylhydroxylamine by Sulphide and Hydrosulphide Ions

Any mechanism for the reduction of nitrobenzene by the $S^=$, SH^- , $S_2^=$ or S_2^- species must explain the following observations.

1. At low hydroxyl ion concentration, as encountered in Goldschmidt's work (52) and where Bullock and Forbes (9) used a borax-boric acid buffer, sulphur is quantitatively precipitated.

2. At higher pH polysulphide is formed, so that at the end of the reduction an overall increase in $S_x^=$ and S_xH^- is observed.

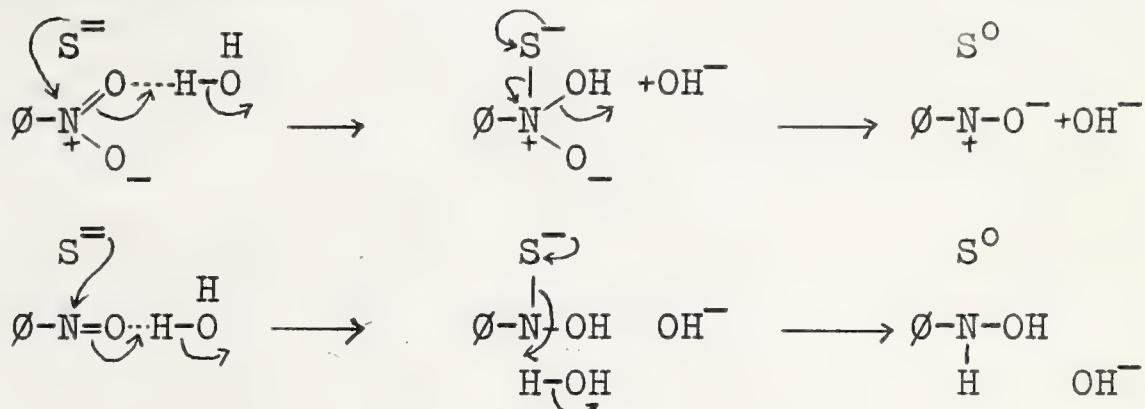
3. In all these reductions there is an initial increase in the hydroxyl ion concentration.

Although no evidence has been offered in this thesis for the presence of nitrosobenzene as a reduction intermediate, this has been assumed in the proposed mechanism below. This is partially by analogy with Haber's work (29) and also because no alternative route can be suggested which, while fulfilling the above three conditions, satisfies the overall stoichiometry of the reduction of nitrobenzene to aniline.

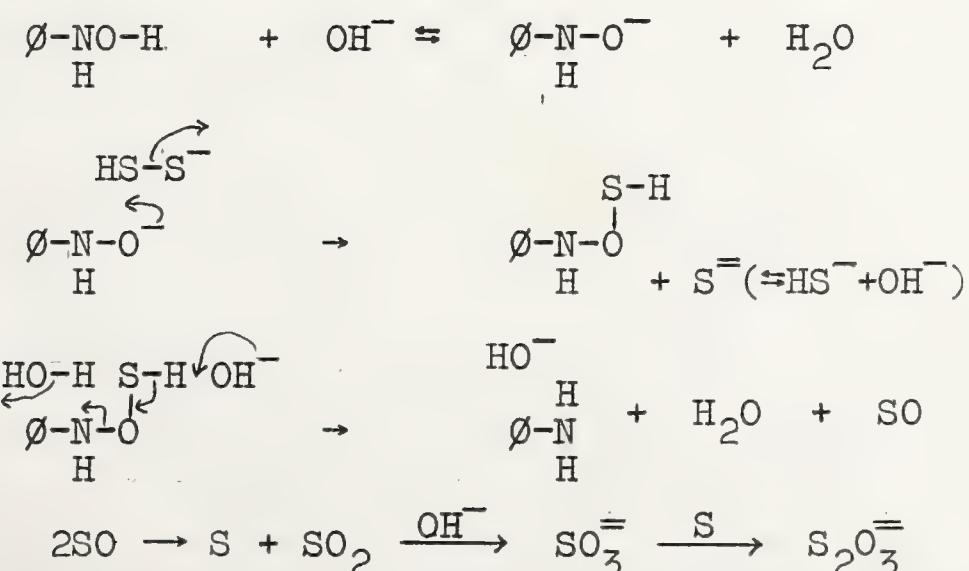
Because of the polarized nature of the nitrogen-oxygen bonds in the nitro and nitroso groups, the nitrogen atom is relatively positive and hence the attack of the negatively charged reducing agent is expected to take place at this atom. It seems likely that attack on the oxygen atom would involve sulphur-oxygen bond formation rather than simply an electron transfer and such a process would account for all the reducing species as sulphite or thiosulphate. Furthermore, it would be difficult to account for the observed pH increase and the stoichiometry by such a mechanism.

The nitro and nitroso groups are considered to be hydrogen bonded to water in the following mechanism. Although the

reaction sequence is only illustrated for the sulphide ion, a similar mechanism is envisaged for the other species. The mechanism is shown as involving nitrogen-sulphur bond formation. However a similar mechanism proceeding by a direct electron transfer process would also explain the observed results.



It is proposed that the final stage involving reduction of the phenylhydroxylamine to aniline takes place via sulphur to oxygen bond formation. This is because the highly polarized N-O bond is now absent and the nitrogen is no longer very positive. Moreover, this explains why phenylhydroxylamine discharges the yellow colour of S_2H^- to give thiosulphate ion. By analogy with the known solubility of oximes in alkali, a pre-equilibrium is proposed involving proton removal. Sulphur-oxygen bond formation follows.



The last equation constitutes a series of known reactions which with the preceding equations accounts for the observed stoichiometry.

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